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WASTE MATERIALS IN CONSTRUCTION

Science and Engineering of Recycling for Environmental Protection

EDITED BY G. R. Woolley • J. J. J. M. Goumans • P. J. Wainwright

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FOREWORD

The Organising and Scientific Committees of the Fourth International Conference on Waste Materials in Construction, in Harrogate, England, on 31 May and 1-2 June 2000, are pleased to present the Proceedings of this Conference which deals with the Science and Engineering of Recycling for Environmental Protection.

SCOPE OF THE CONFERENCE

WASCON 2000 follows on and builds upon the WASCON conferences of 1991, 1994 and 1997. It is focussed on aspects and issues that are relevant to the new millenium and is designed to stimulate debate and promote communication on issues of interest to engineers, scientists, regulators, state and private organisations, and those engaged in the processing and marketing of recycled materials.

The conference provides a European and international communication platform on the important theme of Science and Engineering of Recycling for Environmental Protection. It is a meeting forum to reflect the increasing importance of recycling and re-use of secondary waste materials, proliferation of Research and Development activities and the accumulating amount of information in this sphere of activity world wide.

A number of conference themes have been identified. All are inter-related and inter-dependent in so far that potential users of a secondary, recovered or recycled material have to be assured that the material is environmentally safe and stable. It is the Environmental Challenge that forms a leading theme for the conference, and the themes of Quality Assurance and Quality Control support this aspect. In terms of use of 'recovered' materials, Science and Engineering play important and inter-dependent roles and this is reflected in themes which form the very core of the conference. Of no less importance is Control of Land Contamination and how we propose to model for the Long Term Impact of our aims. However dutiful and competent our ideas and studies, there has to be a measure of control and the Role of Legislation forms the final theme of WASCON 2000.

The Organising and Scientific Committees are encouraged by the excellent response to their call for papers, and we thank all who have contributed to this edition. The breadth of studies being undertaken world-wide and the innovative ideas that are expressed in papers submitted are worthy of this important subject. It is also interesting to note that papers were offered from 30 countries, a sign of the increasing awareness of the need to preserve our natural resources and utilize to the full those with which we are more familiar. We hope that the conference will contribute to the understanding and solution of environmental problems concerning the re-use of waste materials in construction.

ACKNOWLEDGEMENT

Organising a major international conference requires a considerable amount of work for those involved and we would like to express our thanks to the following persons and organisations:

Members of the Scientific and Organising Committees

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2500 GX The Hague, The Netherlands

On behalf of the Organising Committee
Dr Guy R. Woolley

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The following papers were presented as posters:

Waste Materials in Construction
G.R. Woolley, J.J.M. Goumans and P.J. Wainwright (Editors)

Calcium silicate products with crushed building and demolition waste

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The suitability of crushed building and demolition waste as a raw material for the production of calcium silicate products has been determined. Therefore calcium silicate bricks have been produced by replacing natural sand with crushed building and demolition waste of different sources. The mechanical properties of the bricks made with these wastes are comparable or in some cases even better than those of bricks with natural sand. In particular the green shear strength of the bricks is higher. The amount of quartz and reactive SiO_2 in the waste materials is high enough for the formation of tobermorite and hydrogarnet as cementitious materials between the grains. A negative aspect is the appearance of brown stains on the surface of the bricks when the waste materials are slightly contaminated with organic substances. This risk can be reduced by including a washing process, in addition to crushing of the waste.

1. INTRODUCTION

In the Netherlands most of the loadbearing structures in houses are made with calcium silicate products. These products are manufactured with the raw materials sand and lime. After mixing of the raw materials with water and slaking of the lime, the mixture is pressed in the desired shape and autoclaved at about 200 °C. During the hardening process the lime reacts with quartz to form calcium silicate hydrates which give the product the required strength [1]. Products, which do not meet the quality standards, are crushed and are recycled as a raw material for the production of new calcium silicate products.

Building and demolition waste of calcium silicate products is not recycled but crushed, together with concrete and other masonry waste, and re-used in road base courses. The total amount of construction and demolition waste in the Netherlands is about 14 million tons per year; approximately 1 million ton thereof consists of calcium silicate products. In future this way to re-use the building and demolition waste will be more restricted. In order to assure the recycling of these waste products, a study was carried out to use crushed building and demolition waste as a raw material for the production of new calcium silicate products [2].

Calcium silicate industries in Germany [3], Denmark [4] and Switzerland have also studied this subject. The general conclusion of these studies is that possibilities do exist to re-use crushed building and demolition waste as a raw material for the manufacturing of calcium silicate products, but special attention has to be paid to contaminations in the waste materials.

2. MATERIAL DESCRIPTION

The crushed building and demolition wastes (further called aggregates) which are used in this study are all derived from crushing plants. All samples have a grain size ranging from 0 to 4 mm. This range of grain sizes is chosen because the waste is the by-product of the larger grains (4-32 mm) which are used as a coarse aggregate for concrete. Currently these smaller aggregates are not yet re-used as raw materials for building products. Three types of aggregates with different origin are used for this study: aggregates from calcium silicate waste, masonry waste (mainly fired clay bricks and masonry mortar) and concrete waste.

The properties of the aggregates differ from the natural sand, which is normally used as a raw material for the production of calcium silicate products. Some of these properties can have a large influence on the properties of a calcium silicate product made with these aggregates. This is mainly the case for the mineral composition, specific density of the grains, the amount of organic components and the grain size distribution.

The grain size distribution determines the mechanical strength both of the green product and of the hardened product. A uniform grain size leads to a large volume of larger pores in the product. A certain amount of very fine grains is necessary for the chemical reaction during autoclaving [1].

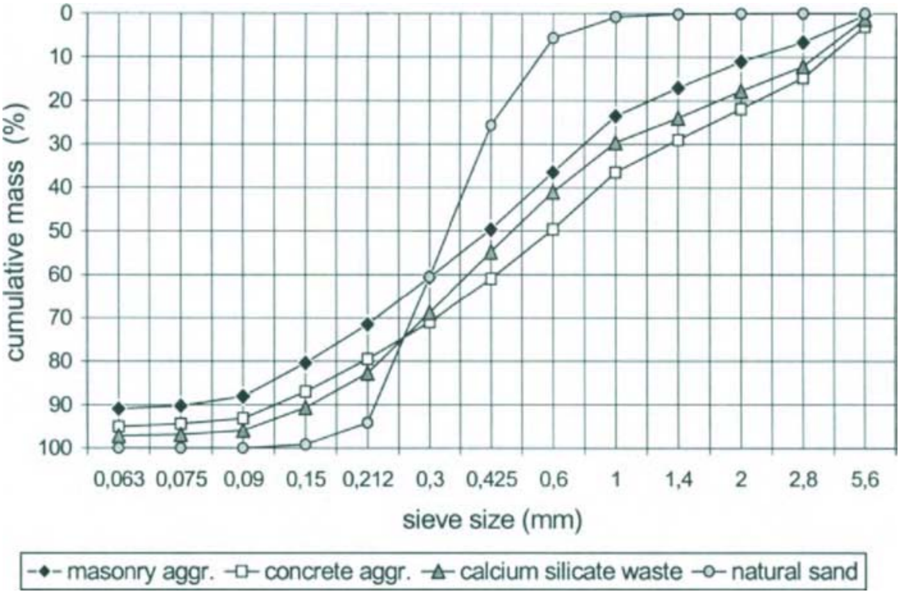

Figure 1. Grain size distribution of aggregates from different waste materials, compared to the grain size distribution of the natural sand.

The grain size distribution of the aggregates (figure 1) is much better graded than the natural sand. These waste materials did not pass a washing step after or before crushing. In some of the aggregates the total organic carbon content is therefore higher than in the natural sands (table 1). However such a content of organic substances is normal for this kind of waste material.

Table 1
Some relevant properties of the crushed building and demolition waste [2].

Material	Specific density of grains > 4 mm (g/cm^3)	Total organic carbon (mass %)	SiO_2 content (mass %)
River sand	2.61	0.05	93.2
Calcium silicate aggregate	1.85	0.08	88.6
Masonry aggregate	1.92	0.34	77.3
Concrete aggregate	2.17	0.50	77.0

The reaction, which takes place during autoclaving of calcium silicate products, needs the presence of lime and of reactive silica with little accessory minerals in the sand. Pure quartz sands seem to be the best raw material for the manufacturing of calcium silicate products, but mainly natural sands have been used throughout the history of the manufacturing of calcium silicate products. The mineral composition of crushed waste materials differs from that of the sands, which are normally used for this purpose. The total SiO_2 content (measured by XRF) is lower in the aggregates than in the natural sand (table 1). For example in fired clay bricks, besides quartz, also different kinds of calcium-aluminium-silicates such as anorthite and gehlenite can be present. The reactivity of the SiO_2 from these minerals is different from that of quartz, which can result in different mechanical properties of the bricks made with this material.

An indicative petrographic study of the aggregates shows however that the fraction < 1 mm of all aggregates consists mainly of individual angular to rounded quartz grains. The fraction > 1 mm contains more crushed concrete, fired clay brick and calcium silicate grains. Because the small grains supply the main part of the reacting SiO_2, this could mean that enough quartz grains are present for the chemical reaction between lime and quartz.

With each of these aggregates, calcium silicate bricks were manufactured on a laboratory scale press. The dimensions of the bricks are 214 x 102 x 50 mm. The realized process conditions are representative of normal production. The following conditions have been realised:

* replacement of the original sand: 0, 20, 50 and 100 %
* lime content: 6.5 mass %
* moulding pressure: 20 MPa
* autoclaving: 4 hours at 200 °C

3. MEASUREMENT OF PROPERTIES

Many properties of the non-hardened and of the hardened bricks have been measured and compared with the properties of calcium silicate bricks in which natural sand is used. Strength and density of the bricks are always given as an average of 6 measurements of individual bricks. Following properties of the bricks were measured:

1. optimum water content of the mixtures in order to obtain a good workability. This is mainly to guarantee the good moulding of the mixtures.
2. green shear strength, measured as the strength necessary to push a small cylinder out of a larger cylinder of a moulded mixture. A good green shear strength is necessary for the transport of the products within the factory before hardening.
3. bulk density, measured by determination of weight and dimensions of the bricks. A minimum dry bulk density of about 1700 kg/m^3 is regarded necessary to obtain good sound insulation properties of the wall structure.
4. three point flexural strength. This property is not specified in the building regulations, but gives additional information to the mechanical properties.
5. compressive strength, measured on a hydraulic press. The compressive strength of the bricks should be at least 15 MPa, but preferably more than 25 MPa.
6. mineral assemblage of the cementitious materials between the sand grains, determined with X-ray diffractometry (XRD).
7. pore size distribution of the bricks by mercury intrusion porosimetry (MIP).

4. RESULTS

In order to mould the mixture into a desired shape, a certain workability is required. In this case the workability is defined as the pressure needed to obtain a certain bulk density and green shear strength of the non-hardened brick. Due to a higher water absorption of the aggregates compared to the natural sand, the mixtures with aggregates need a higher water content than the mixture with natural sand. The regular mixture of natural sand, lime and water, before moulding, contains about 4 % of water. The preferred water content gradually increases to about 12 % with a total substitution of the sand by aggregates (table 2). All properties of calcium silicate bricks, which will be discussed, have been determined on samples with similar workability, but therefore different water content before moulding. Generally this does not affect the mechanical properties of the products.

Using a set moulding pressure of 20 MPa, the moulded but non-hardened bricks show different bulk densities (table 2). With the use of masonry- and concrete aggregate the bulk density does not change much up to 50 % sand replacement, and only shows a slight decrease when all the sand is replaced by aggregates. This can be explained by a combination of a lower specific density of the aggregates and a more favourable grain size distribution of the aggregates compared to the natural sand (figure 1). Replacing the sand by calcium silicate aggregate leads to a larger decrease of bulk density (from 1740 to 1630 kg/m^3 going from 0 to 100 % sand replacement). The bulk density as obtained by replacing the natural sand completely with calcium silicate aggregates is rather low for the application of this kind of brick.

Table 2

Properties of calcium silicate bricks with varying types and amounts of crushed building and demolition waste. KZ = calcium silicate waste, BA = masonry waste, BE = concrete waste, CV = coefficient of variation.

Property	Ref.	KZ			BA			BE		
Aggregate amount (mass %)	0	20	50	100	20	50	100	20	50	100
Water content of green mixture (mass %)	4.0	5.2	7.0	11.8	5.2	7.0	12.2	5.6	8.0	14.0
Bulk density (kg/m^3)	1740	1710	1700	1630	1740	1740	1700	1740	1760	1720
Green shear strength (MPa)	0.50	0.92	1.75	2.10	0.92	1.58	2.82	0.95	1.41	1.97
CV	0.01	0.08	0.03	0.09	0.06	0.05	0.10	0.05	0.03	0.25
Flexural strength (MPa)	3.3	4.2	4.4	2.2	4.9	5.6	5.7	4.1	5.0	5.2
CV	0.4	0.4	0.1	0.1	0.4	0.3	0.3	0.4	0.3	0.2
Compressive strength (MPa)	32.3	32.0	32.8	22.6	35.7	39.2	40.9	36.6	38.5	34.8
CV	0.4	0.9	0.4	0.2	0.7	0.5	0.6	0.6	0.7	0.9

Due to the broad grain size distribution and the angular shape of the aggregate grains, the cohesion between the grains in the moulded and non-hardened bricks is larger than the cohesion between sand grains. The green shear strength therefore increases strongly with increasing aggregate content. Bricks with total substitution of sand by aggregates have the highest green shear strength. In most cases a higher green shear strength leads to a decrease of product loss in the production plant. The use of aggregates from building and demolition waste therefore seems to provide a good possibility to optimise the efficiency of the production process.

When the natural sand is replaced by masonry or concrete aggregates the flexural strength of the bricks increases gradually with increasing aggregate content (table 2). Only when the natural sand is replaced by calcium silicate aggregates there is a sharp decrease of the flexural strength between 50 and 100 % replacement. Here a relation with the decrease in bulk density can be noticed. A similar trend can be seen for the compressive strength. The replacement of natural sand with 100 % calcium silicate aggregate also leads to a lower compressive strength. This strength is even lower than 25 MPa, which is the target compressive strength. A reason for this reduction of strength could be that the quartz grains in the calcium silicate waste are partly covered with calcium silicate hydrates. On these spots the access to the silica source is restricted. However, the decrease in bulk density and the difference in grain size distribution of the different aggregates might also be factors which explains a lower strength when using calcium silicate aggregates in stead of masonry or concrete aggregates. Bricks made with masonry or concrete aggregates have a higher or comparable compressive strength as the regular calcium silicate bricks.

Some organic substances in the aggregates, such as bituminous components, dissolve partly during autoclaving and are transported to the surface of the brick. When the sand is replaced by aggregates with a slightly higher content of organic carbon, this leads to brown stains on the surface (figure 2).

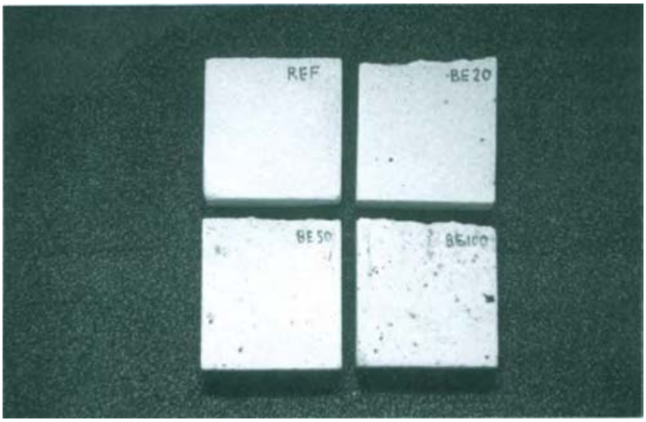

Figure 2. Calcium silicate bricks made with 0, 20, 50 and 100 % replacement of sand by crushed concrete waste. Brown stains occur due to a very small amount of organic substances in the waste.

Small pieces of wood enhance the formation of local fissures in the brick. The appearance of bricks with such brown stains cannot be accepted and poses a great disadvantage to bring such products on the market. Bricks with calcium silicate aggregates have only a few brown stains because of a low organic carbon content of the aggregate.

Although different cementitious minerals could be expected using aggregates with a different mineral composition, the XRD patterns show tobermorite and hydrogarnet as cementitious materials in the bricks [5]. The amount of tobermorite and hydrogarnet increases with increasing amount of waste aggregates. Figure 3 depicts the XRD pattern of bricks with substitution of sand by concrete aggregate.

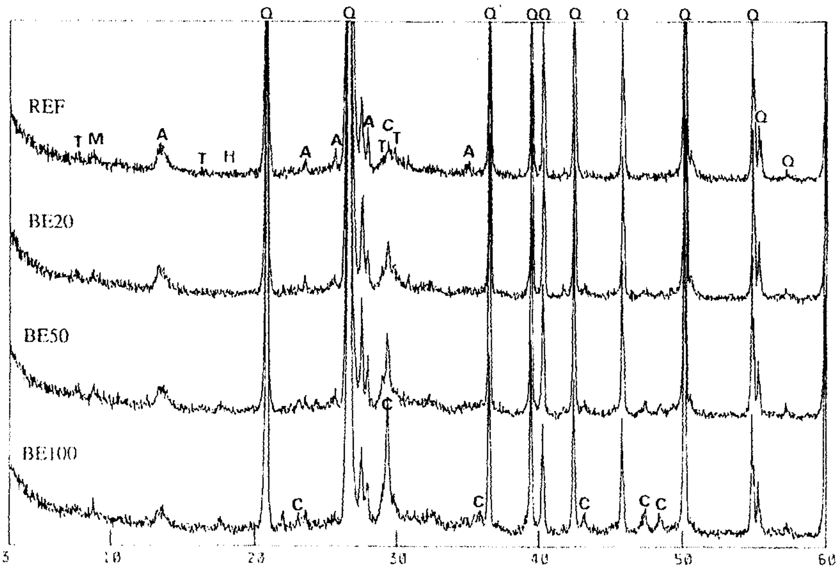

Figure 3. XRD pattern of calcium silicate bricks made with 0, 20, 50 and 100 % replacement of sand by crushed concrete waste. T = tobermorite, C = calcite, Q = quartz, M = muscovite, A = albite, H = hydrogarnet.

Bricks with other aggregates do not differ much from this pattern. Relating to the acquired strength of the bricks, it is clear that the formation cementitious binder is sufficient for good mechanical properties of the bricks. Also the amount of calcite ($CaCO_3$) rises with increasing replacement of sand by the aggregates. The calcite is already present in the aggregates and originates from the carbonation of building materials such as masonry mortar, concrete and calcium silicate bricks.

Figure 4 shows the pore size distributions of some of the bricks. All bricks show an increase of pores < 1 μm with increasing aggregate content. This coincides with a decrease of pores > 10 μm, mainly due to a better packing of the grains as a result of a better pore size distribution of the aggregates compared to the natural sand. The total pore volume slightly increases with increase use of calcium silicate aggregate and decreases with increased use of concrete aggregate. The pores in the bricks correspond mostly to the newly formed pores and only partly to pores in the coarse grains of the aggregates.

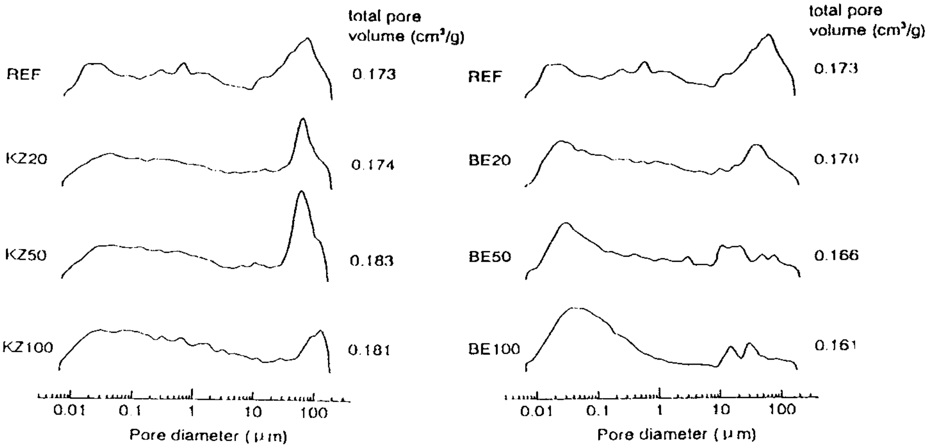

Figure 4. Pore size distributions of calcium silicate bricks with 0, 20, 50 and 100 % replacement of sand by crushed building and demolition waste materials. KZ = calcium silicate waste, BE = concrete waste.

5. FULL SCALE EXPERIMENTS

The laboratory study indicates that a good quality aggregate from building and demolition waste could be used as a raw material for the production of calcium silicate products. However, some aspects concerning the production of calcium silicate products can only effectively be determined in a manufacturing plant. This accounts mainly for variations in the water content and the workability of the mixtures and partly for variations in the mechanical properties of the products. Therefore, at one of the Dutch plants calcium silicate blocks (30 x 20 x 15 cm) have been produced using about 50 tons of aggregates from calcium silicate waste and aggregates from mixed masonry and concrete waste. The aggregates will further be called calcium silicate aggregate and mixed aggregate. Both aggregates have been obtained by crushing the building waste and demolition waste and sieving a coarse fraction (0-20 mm) on a 4 mm screen, thus obtaining aggregates with a grain size of 0-4 mm. Because the laboratory study indicated that the content of organic substances has a negative effect on the appearance of the brick, the mixed aggregate was washed at the crushing plant. The washing process was carried out with an Alljig 2022. The organic carbon content after washing is 0.16 % (m/m), which is less than the organic carbon content in the masonry and concrete aggregates which were used in the laboratory tests.

Mixing and moulding of the mixtures and the autoclaving of the green products followed standard procedures, using the equipment, which is also used for the production of regular calcium silicate products. The natural sand has been replaced with 10, 30 and 50 % of calcium silicate aggregate and with 50 and 100 % of mixed aggregate. The lime content of all mixtures is 7 %. The moulding pressure has been kept as constant as possible at 11 ± 0.5 MPa. All blocks, which were produced during the test, have been hardened in one single autoclave during 4.5 hours at 200 °C. During the production process of the blocks no obstructions have been seen which hindered the process. Some properties of the calcium silicate blocks are shown in table 3.

Table 3
Properties of calcium silicate blocks manufactured in a calcium silicate plant with crushed building and demolition wate. KZ = calcium silicate waste, MX = mixed masonry/concrete waste, CV = coefficient of variation [2].

Property	Ref.	KZ			MX	
Aggregate amount (mass %)	0	10	30	50	50	100
Water content of green mixture (mass %)	4.7	5.4	5.9	7.8	7.6	9.3
Bulk density (kg/m^3)	1780	1780	1760	1770	1750	1770
Green shear strength (Mpa)	0.40	0.52	0.76	1.56	0.45	0.58
CV	0.01	0.04	0.04	0.10	0.05	0.02
Compressive strength (Mpa)	25.4	28.4	17.9	16.4	24.0	22.1
CV	2.5	2.7	1.5	4.5	2.4	0.8

In order to reach a comparable workability of the mixtures, the optimum water content increases with increasing aggregate content. At a higher level of replacement this is lower than which could be seen from the laboratory tests. The bulk density of the blocks does not vary much with increasing aggregate content. As in the results of the laboratory tests, the green shear strength increases with increasing aggregate content, although the green shear strength of blocks made with mixed aggregate is much lower than that measured in the laboratory tests. A reason for this lower shear strength is not yet clear. The laboratory test showed that the compressive strength of bricks with calcium silicate aggregates decreases rapidly above 50 % replacement of the natural sand.

In the full scale test this decrease of compressive strength occurs already at 30 % replacement of the sand with no significant change in bulk density. This means that the target compressive strength of 25 MPa is not reached for these mixtures. This is a restriction of the application of such products. Also in this case the difference with the laboratory test results has yet to be clarified.

The appearance of the blocks made with the (washed) mixed aggregate is tolerable. Only a few brown stains can be seen at the surface of the blocks. In the calcium silicate aggregate small bituminous components from roofing material and asphaltic concrete can be seen. The result of this contamination can be seen at the surface of the blocks made with these aggregates. Many brown stains such as depicted in figure 2 can be seen, especially in blocks made with 30 and 50 % calcium silicate aggregate. This appearance cannot be accepted for products, which have to be commercialised.

A warning for the use of crushed building and demolition waste materials as a raw material for the production of building materials comes from a study carried out by the Dutch road and hydraulic engineering division [6]. In this study a mixed aggregate (0-4 mm) has been used in a full scale experiment to replace sand as an aggregate in concrete. With the regular use of this mixed aggregate caking and clogging of the material in the bunkers occurred. This slowed down the production process considerably. This is probably due to a reaction between non-reacted cement particles (at the surface of the aggregates after crushing) and water. This risk is even more present when producing calcium silicate products. Before moulding, the mixture is stored for 1 to 2 hours in a bunker in order to allow for the slaking of lime. Temperatures in these bunkers reach about 70 °C. This can accelerate the chemical reaction between cement and water. When only calcium silicate waste materials are used this risk can be minimised, because of the absence of cement in this material. During the full-scale test no problems of this kind occurred, but the storage time in the bunker has in these test been minimized to 30 minutes.

6. CONCLUSIONS

Replacing natural sand by crushed building and demolition waste for the manufacturing of calcium silicate products can give products with mechanical properties, which are comparable or even better than the original products. Mainly the increase of the green shear strength with increasing amount of crushed waste materials is notable. This could lead to a decrease of product losses during the manufacturing process. Replacing the natural sand with 30 % or more crushed calcium silicate waste notably lowers the flexural and compressive strength of the products, while replacement with crushed masonry or concrete waste gives compressive strengths, which are comparable or higher than the strength of regular calcium silicate products. This means that the aggregates contain enough reactive silica for the formation of cementitious materials (such as tobermorite and hydrogarnet) between the grains.

A negative aspect is the appearance of brown stains on the surface of the calcium silicate products when sand is replaced by crushed building and demolition waste which is contaminated with even a small amount of organic substances. Only crushed waste materials, which passed a washing process, are therefore suitable as raw materials for the production of calcium silicate products.

In a full-scale test no problems occurred during the production of calcium silicate blocks, replacing the sand partly with crushed calcium silicate waste or even completely with crushed masonry and concrete waste. However, a warning is given for a possible clogging of equipment during continuous use of these aggregates, due to the hydration of cement particles in crushed concrete or mortar.

From this study it can be concluded that the use of crushed building and demolition waste as a raw material for the production of calcium silicate products is a viable option, when the contamination of organic substances is minimized. A feasibility study of a logistic system for the transport of waste materials from the building and demolition site, via a crushing plant, to the calcium silicate plant is necessary.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Predicting strength properties of fine cementless fly ash - furnace bottom ash concrete

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Methods for predicting strength properties of cementless ash – slag concrete for the long term have been developed at the Siberian State University of Industry. Data from a 10 – year study of an ordinary heavy concrete as compared with a cement concrete containing ash from thermal power plants were taken for analogies. The methods were as follows:

1. predicting based on the dynamics of the analog of the object for prediction using the method of similarity,
2. predicting based on the dynamics of the object indices in the "accelerated" time scale.

The first method included monitoring the dynamics of indices of the analogs of the object for prediction, monitoring the dynamics at the initial (limited) time period of the object functioning, determining coefficients of similarity, and predicting the object indices by affinal transformations and recalculations according to the similarity criteria. The second method consisted in obtaining the dynamics of the indices of the object analog functioning in the "accelerated" time scale, that is exposed to contrast loadings much more frequently than during the normal object functioning.

1. INTRODUCTION

As a result of a long-term investigation, the Siberian State University of Industry has developed compositions and technologies for fine cementless concrete from wastes of thermal power plants (high – calcium ash and slags from combustion of the Kansk Achinsk Thermal Power Complex) and steel industry, 15 to 30 MPa strength classes. The patented concrete mixture (patent # 2065420) has the following mixture proportions: 30 to 40 % high – calcium ash 30 to 40 % slag sand of up to 5 mm size fraction, 5 to 10 % silica fume and water with a temperature of 60 to 80 ^{0}C (1, 2).

The data on its durability, including physico-mechanical and deformation characteristics over a 5 – year period (3), frost resistance, waterproofness, corrosion resistance, chemical, radiation and fire resistance, were published elsewhere (4). This paper presents the results of the study of the general durabiliy indices of fine cementless concrete performed in the usual (non - aggressive) environment as well as the prognosis of its service life compared with ordinary heavy concrete and concrete containing ash from the combustion of Kuznetsk coals.

2. FINE CEMENTLESS CONCRETE MIXTURE READY FOR USE

2.1. Materials

Fly Ash. According to the classification of Ivanov (5), high – calcium fly ash from the Abakan thermal power plant is a coarse dispersed powder of a light brown color with a surface area of 238 m^2/kg. Its particles being agglomerated, it has to be ground in ball mills to a surface area of 450 m^2/kg. Its bulk and absolute densities are 1200 and 2350 kg/m^3, respectively. The chemical analysis of fly ash is given in Table 1.

Furnace bottom ash sand. Furnace bottom ash sand is produced by grinding the coarse ash from the above source in a roller crusher to a particle size of 0 to 5 mm. Crushing destroys weak (with microcracks) particles and doubles frost resistance of this sand. Its bulk and absolute densities are 1400 and 2450 kg/m^3, respectively. The chemical analysis of the furnace bottom ash sand is given in Table 1.

Silica Fume. Silica fume is a by-product from the Kuznetsk ferroalloy plant of a light grey colour with a surface area of 2200 to 3000 m^2/kg. Its chemical analysis is given in Table 1.

Optimum Mixture Proportions:
Fly ash – 1000 kg/m^3
Furnace bottom ash sand– 1000 kg/m^3
Silica fume – 70 kg/m^3
Water – 400 kg/m^3

2.2. Properties

Properties of the mixture and concrete are given in Tables 2 and 3.

Following examination by leading Russian institutions in the field of concrete, the concrete mixture was awarded *"Technical Certificate № -07-0175-99"* for the use of the product in the Russian Federation as well as the applicability mark.

Field experience showed that fine cementless ash – slag concrete can be used as commodity mixtures for load – bearing structures constructed in a non – aggressive environment.

In association with the Laboratory of Corrosion, NIIZhB, the ability of a new concrete to resist corrosion of reinforcement was investigated. It was found that steel was safely protected in a dense ash – slag concrete. Electrochemical tests were made in accordance with State Standard 4421-88 on 70x70x140mm specimens reinforced with steel wire 6mm in diameter and 120mm long. The test results are given in fig.1.

It is evident from the data of fig.1 that steel in a cementless concrete was passive during all period of testing. The pH values of a liquid phase (11.87 and 11.85 in the initial state and at 6 months, respectively) also give an indication of a passivating effect of concrete on the reinforcement.

Table 4
Mixture Proportions and Physical Properties of Concretes with without Ash and of Cementless Concretes

Concrete type	Quantities, kg/m^3					Slump, cm	Compressive strength, MPa		Average density, kg/m^3
	Class 400 PC	Sand	Rubble	Ash	Water		28 days	1500 days	
Heavy concrete without ash	375	655	1220	-	200	10	20.5	25.5	2423
Concrete with fly ash from the West – Siberian TPP	280	530	1100	200	240	22	22	33.1	2325
Concrete with fly ash from the South – Kuzbass power plant	280	530	1100	200	240	20.5	20.5	34.7	2275
Fine cementless fly ash – furnace bottom ash concrete with high – calcium ash from the Novosibirsk TPP	High – calcium ash	furnace bottom ash 0…5 mm in size	-	Silica fume	Water	10	15.2	22.08	1900
	615	720	-	105	480				
Fine cementless fly ash – furnace bottom ash concrete with high – calcium ash from the Abakan TPP	622	830	-	83	415	10	15.8	21.2	1980

Table 5
Compressive Strength Development of Concretes

Concrete type	Compressive strength of Concrete at the days of testing, MPa							
	28	100	200	300	400	500	1100	1500
Ordinary heavy concrete without ash	20.5	20.8	21.9	22.6	23.2	23.7	24.8	25.5
Heavy concrete with fly ash from the West – Siberian TPP	29.7	30.1	32.7	33.6	36.2	41.2	41.2	42.4
Heavy concrete with ash from the South – Kuzbass power plant	28.0	28.3	35.5	36.8	40.0	43.0	44.0	44.2
Fine cementless fly ash – furnace bottom ash concrete with high – calcium ash from the Novosibirsk TPP	15.2	15.91	16.67	17.41	18.15	19.79	20.96	22.08
Fine cementless fly ash – furnace bottom ash concrete with high – calcium ash from the Abakan TPP	15.8	16.4	21.2	21.2	21.2	21.2	24.9	

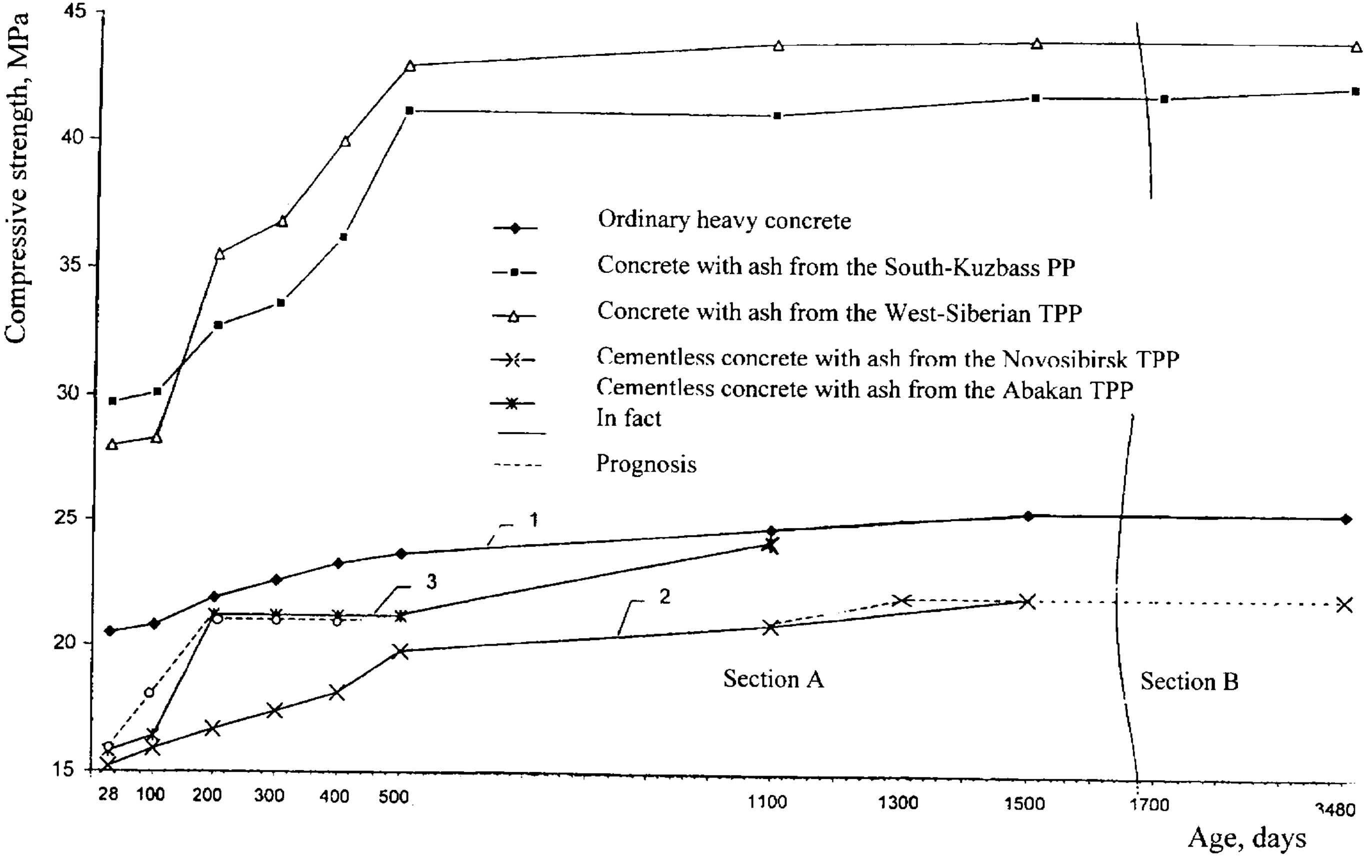

Fig. 1. Compressive strength of concrete versus age

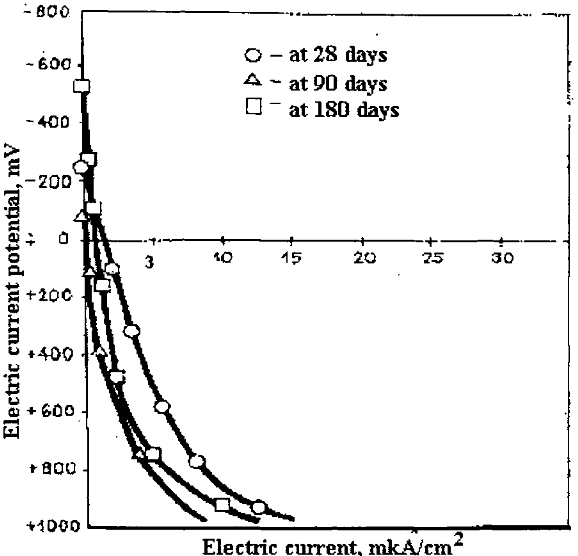

Fig.1. Anodic polarisation curves for cementless fly ash-furnace bottom ash concrete

3. METHODS OF PREDICTING STRENGTH PROPERTIES OF CEMENTLESS CONCRETE

To gain in information on the durability of a new concrete, methods for predicting strength properties over an extended period were developed. Data from a 10-year investigation of heavy concrete as compared with concrete containing ash from thermal power plants (6) were taken as analogs. Mixture proportions and properties of concretes are given in Table 4. Strength development with respect to time is given in Table 5.

It was established that for a 10-year period, ordinary heavy concrete and concretes with a higher ash content had a 24, 43 and 58 % (at above 30 percent cement saving) strength gains, respectively, while for the period from 500 to 1500 days, cementless concrete with ash from the Novosibirsk and Abakan thermal power plants had a 34 and 45 % strength gains, respectively. The investigation showed that cement concretes with a higher ash content had a greater potential for strength gain with respect to time than ordinary and cementless concretes. For example, concrete with ash from the Abakan thermal power plant ceased developing strength at 3 months exhausting the binding potential of the ash. The coefficient of quality (C_q) of this ash (1.13) is lower than that of the ash from the Novosibirsk thermal power plant (1.5), where Cq is an index determined by State Standart 3476 for evaluation of binding properties of high-calcium ashes and slags; the Cq>1 indicates that ash has binding properties. Further research on prognosis of their durability is needed.

Table 1
Chemical Analysis of Fly Ash, Furnace Bottom Ash and Silica Fume

Oxides	Components		
	fly ash	furnace bottom ash	silica fume
IO$_2$	40.47	50.47	9048
CaO total	34.94	29.92	2.12
Including free CaO	15.75	-	-
MgO	7.18	3.50	0.86
Al$_2$O$_3$	4.57	8.16	0.99
Fe$_2$O$_3$ + FeO	11.02	9.63	3.55
K$_2$O + Na$_2$O	1.08	-	0.35
SO$_3$	0.25	0.01	0.87
TiO$_2$	0.09	-	-
MnO	0.17	0.18	0.20
LoI	1.65	-	1.25

Table 2
Properties of Fly Ash – Furnace Bottom Ash Mixture

Slump, cm	Workability VS time, Slump, cm, Min			Segregation, %	Air – entrainment, %
	15	30	60		
3	1.8	1.0	0.2	2.0	1.5

Table 3 – Physical Properties of Hardened Mixture (Concrete)

Properties	Age testing, days	
	1 day	28 days
Compressive strength, Mpa	10	25
Relative shrinkage, mm/m		0.35
Frost resistance	F25	F50

The methods for predicting strength properties of cementless concrete were developed in two directions:

1. Predicting based on the dynamics of the analog of the object for prediction using the method of similarity,
2. Predicting based on the dynamics of the analog of the object indices in the "accelerated" time Scale.

The first method included the following operations:

a) monitoring the dynamics of the indices of the analog of the object for prediction,
b) monitoring the dynamics of the object for prediction at the limited initial section of the object functioning,
c) determining the coefficient of similarity (time-scale factors, scaling etc) for the initial sections of functioning of the analog and the object for prediction,
d) predicting the object indices by affinal transformations (7) and recalculations according to the similarity criteria.

Application of the combined statistic analysis schemes (8), when characteristics of the indices of the object for predicting are searched by means of the statistic characteristics determined at the initial section and also statistic characteristics for the object analog indices, may serve as the modification of the above technique.

The second method consisted of the following operations:

a) obtaining the dynamics of the indices of the object analog functioning in the "accelerated" time scale, e.g. exposed to contrast loadings much more frequently (by scores of times) than during the normal object functioning,
b) determining coefficients of the time scale and similarity criteria variation,
c) predicting by means of the deformation (unrolling) of the object analog indices dynamics using the coefficients of the time scale and similarity criteria variation.

Here is an example to illustrate the methods described.

There is:

- temporal sequence of the strength development of ordinary heavy concrete over the period of 3480 days (curve 1 in Figure 1),
- temporal sequence of the strength development of fine cementless fly ash – furnace bottom ash concrete with high – calcium ash from the Novosibirsk thermal power plant № 3 over the period of 1500 days (curve 2 in Figure 1),
- temporal sequence of the strength development of fine cementless fly ash – furnace bottom ash sand concrete with high – calcium ash from the Abakan thermal power plant (curve 3 in Figure 1).

It is necessary:

- to predict the value of the compressive strength for cementless concrete with ash from the Novosibirsk thermal power plant for the period of up to 3480 days as well as for concrete with ash and furnace bottom ash from the Abakan thermal power plant for a much longer period.

The first method is used for predicting provided the analog (ordinary heavy concrete) and the objects (cementless concretes with fly ash and furnace bottom ash from the Novosibirsk and Abakan thermal power plants) have similar physical characteristics.

For concrete with fly ash and furnace bottom ash from the Novosibirsk thermal power plant, the coefficient of time scale $C_t = 1.0$ and the index variation velocity coefficient $C_v = 1.25$ were calculated at the section A. According to these coefficient values, the dynamics of the strength development for the period of 3480 days (dotted line in curve 2) was predicted. The prognosis was made by taking into consideration the facts that the analog concrete had already achieved its ultimate strength by the period of 1500 days while concrete being predicted was to gain its strength limit by 1.25 time faster, that is by the period of 1300 days.

For concrete with fly ash and furnace bottom ash from the Abakan thermal power plant, the scale coefficient of time was calculated as the relation between the strength development intervals for concrete being predicted and those for the analog concrete ($C_t = 7.5$). Prediction was made by means of the temporal deformation of the curve 1 by 7.5 times. The results of the prognosis are illustrated in Figure 1 (curve 3, dotted line). It should be noted that by compression of the curve 1, the prognosis could only be made for 450 days. Nevertheless, the analysis of the results obtained gives every reason to speak about the satisfactory accuracy of the prognosis.

For the above case, we managed to make the prognosis of the dynamics of the curve 1 on the basis of the dynamics of the curve 3. It was made possible by means of the scale factor determined which "extended" the second part of the curve 1 (beyond sector A) by 7...5 times, that is to 375 days more.

4. CONCLUSIONS

1. The methods of predicting service life of new concretes over an extended period seem to be encouraging in terms of their perspective and profitability.
2. The method is to be developed by involving mathematical procedures of fractal geometry and complex statistic characteristics. Application computer programs should be compiled.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Development of utilization technologies for Mt. Pinatubo ejecta as prime material for concrete: Part 1- Concrete material structure-property characterization

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A total of 11 billion cubic meters of volcanic materials was ejected by the Mt. Pinatubo after its 13 major blasts from 1991 to 1994. This is considered as one of the most devastating disaster of the decade. The deposits are predominantly pumiceous of andesite scoria, with phenocryst-rich and phenocryst-poor dacite pumice fragments. Due to the large volume of volcanic debris, government and private institutions are looking for ways to utilize and maximize the economic potential of these materials. A medium term R&D Program was developed in order to come-up with utilization technologies of Pinatubo ejecta for the construction sector, and that will tackle basic questions of raw material sourcing, material optimization, design and tests of product for specific applications, validation, and transfer of technology to adoptee. The Technological University of the Philippines in cooperation with Nihon University, Japan's Ministry of Education, and Philippines' Department of Science and Technology launched an R&D program on utilization of Mt. Pinatubo ejecta for construction. The objective of this research program is to provide a comprehensive experimental and analytical characterization of Pinatubo ejecta material for various applications in the construction. This paper describes the significant results of extensive studies conducted by the authors in 1991- up to present in the following areas:

1. Structure-Property characterization of ejecta material
2. Application as prime material replacement for cement for durability improvement
3. Application for lightweight concrete and mix designs proportions

1. INTRODUCTION

The June 1991 eruption of the Pinatubo volcano is one of the most devastating disasters in the Philippines this decade. Even at present, the intermittent discharge of ejecta with water continuously brings havoc and destruction to the nearby provinces. The Mt. Pinatubo is located at 15°8'N and 120°21'E lies in the boundaries of Pampanga, Zambales and Tarlac, and it is a part of the chain of volcanoes in the western side of Luzon. The Pinatubo is about 150 km away from Manila but in its history of 13 major blasts events, aerosol clouds of the eruptions were heavily felt even in Metro Manila. The total volume of materials ejected by the Pinatubo is about 11 billion cu.m., enough to cover the whole City of Metro Manila in 18-meter deep ash. In order to cope with the problems of the Pinatubo eruptions and volcanic debris flow, various government and private agencies are continually exerting efforts and conducting scientific studies to minimize its devastation. The volcanic deposits are currently being studied and developed for various applications in agriculture, ceramics, foundry works, textile industry, entomology, soil and pavement engineering, civil and construction works, and material science (Agron,1997; Baarde, 1996; Pagbilao et al, 1994; Jorillo et al, 1996; Ignacio et al, 1994).

The absence of a holistic approach on the utilization technology of Pinatubo materials for the construction industry warrant an R&D program which will tackle basic questions of raw materials sourcing, material optimization, design and tests of product for specific application, validation, and transfer to technology adoptee. Also, there is very little in-depth information available on the properties of concrete with Pinatubo ejecta as a constituent material, especially in the areas of :

1. Structural mix design proportion with property characterization
2. Long-term strength development
3. Full scale applications

With these identified needs, the Integrated Research and Training Center of the Technological University of the Philippines together with the College of Science and Technology of Nihon University, and PCIERD of the Department of Science and Technology launched an R&D program on the utilization of Pinatubo as a material for construction. The objective of the program is to develop cost-effective means of utilizing Mt. Pinatubo volcanic ejecta for the construction industry. The conceptual framework of the program is summarized in Fig. 1. The general experimental program analyzes different material parameters and methods to determine the structure-property of Pinatubo ejecta. The flowchart considers all-important variables, which will respond to the requirements of structural, and materials design. From here, empirical relationships and design tables were derived, and further validated through design and test of a structural wall element.

Specifically, the objectives of the program are,

a) Evaluate the structure-property of Pinatubo materials,
b) Evaluate the suitability of Pinatubo ejecta as a pozzolanic material
c) Determine the durability properties of Pinatubo-based materials and products,
d) Determine the suitability of Pinatubo ejecta as an aggregate constituent of concrete and cement-based products, and

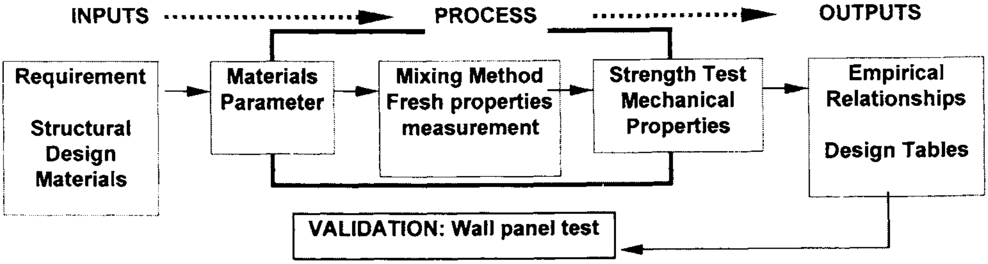

Figure 1. Conceptual framework of the experimental design

2. CHARACTERIZATION OF THE STRUCTURE-PROPERTY OF PINATUBO EJECTA

The first challenge imposed by a new material in order to advance its utilization by the industry is quantity and quality assurance, and comprehensive scientific characterization

Quantity and Quality Assurance reflects the concerns on the fluctuation of quality along with homogeneity of the volcanic deposit as it is directed towards an industrial product or process utilization.

Comprehensive Scientific Characterization of the ejecta would enable the material scientist and engineers to devise methods, processes, and design on utilization technologies most appropriate for the peculiar property of the material.

1.1. Sampling of Pinatubo ejecta

The Project Team performed an extensive visual inspection around the Pinatubo area from 1994 to 1996. Sites inspected in Pampanga were Pasig-Potrero, Lubao, Mabalacat, and Angeles. In Tarlac province, areas of Bamban and Sacobia, while for Zambales, San Felipe, Sto.Tomas, and Botolan. Figs. 2 and 3 show the geographical locations and sites where inspection and sampling were executed. The physical properties of samples per ASTM and JIS procedures are shown in Table 1.

1.2. Physical properties of fine aggregates

Evaluation of the physical properties were made using ASTM methods or JIS whenever applicable. The results showed the following:

- Specific gravity varies from 1.90-2.45, and this variation depends on the particle size distribution, i.e., fine material approaches a specific gravity of 2.45 while it was 1.25 for larger particles
- Has high fine sand composition (0.150-0.075 mm) varying from 5-20% beyond the 10% maximum requirement of ASTM C-33 for fine aggregates for concrete. This may result in higher binder requirement due to its high specific surface area
- Has high water absorption ranging from 2-10%, which would also result in higher water requirement
- Unit weight of sand is relatively lighter compared to ordinary local river sand. It ranges from 1200-1500 kg/m^3.
- The Pinatubo sand is highly friable especially for larger particles of 2.5-5mm

1.3. Physical properties of coarse aggregates

General observation drawn from results is as follows:

- Sampling showed that the coarser components vary from 20-40% depending on sites (proximity to the vents) and dryness of the materials. It appears that the vicinity where coarse aggregates are more abundant is those quarry sites nearer the Pinatubo vents.
- Specific gravity of sizes ranging from 10 to 25 mm is about 1.2-1.35. The water absorption ranges from 24-32% - wide variation in the absorption is brought about by the difficulty of extracting an exact saturated-surface dry (SSD) condition for a porous aggregate such as pumice stones.
- Unit weight ranges from 600-700 kg/m^3, which is a good property for lightweight aggregate

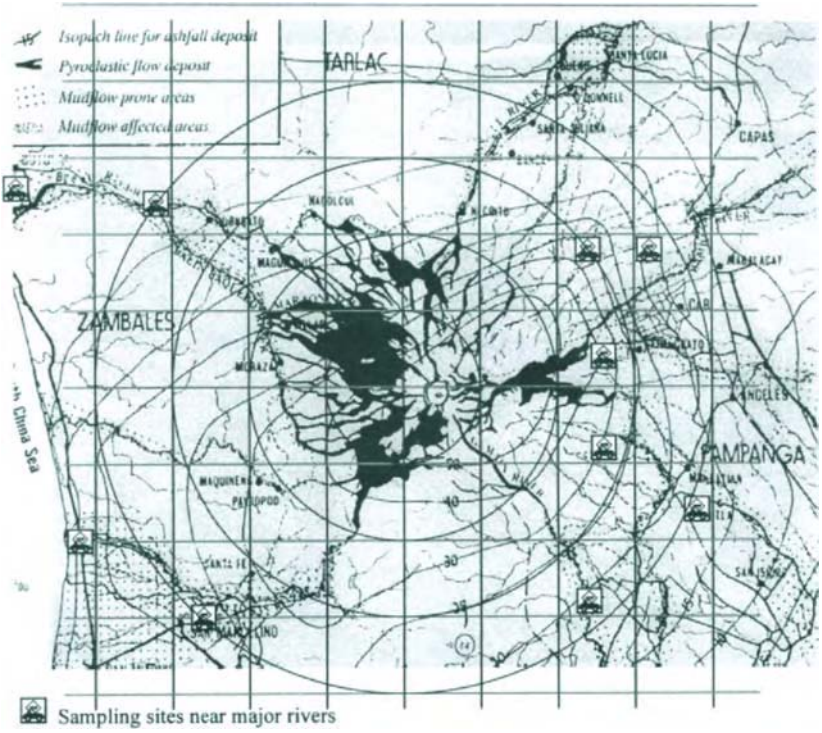

Figure 2. Pinatubo Vicinity map in 10 km grid scale indicating sampling sites

- Coarse aggregates are highly friable and porous.
- Due to wide variation in size distribution, it is recommended that size groupings should be carried out to maintain consistency in the size distribution.

1.4. Chemical and mineralogical properties

- SiO_2 is of relatively large percentage, 58-65%, which is a good index of possible pozzolanicity. The close range of SiO_2 values is reflective of the uniformity of the mineralogical property of Pinatubo, unlike the coal fly ash with a SiO_2 range of 30-80%.
- The Al_2O_3 and Fe_2O_3 range is likewise close which is an indication of the apparent homogeneity of chemical composition regardless of site and time of sampling
- The SiO_2: Al_2O_3 characterization ratio ranges from 3.1 to 4.0 indicating its suitability for cement addition
- The $SiO_2+Al_2O_3+Fe_2O_3$ composition ranges from 79-88%, which is well above the chemical requirement set by the ASTM C-618 specification for natural pozzolans
- The alkali limit requirement (optional chemical requirement) of 1.5% set by ASTM were exceeded by all Pinatubo samples, where the Na_2O ranges from 2-5% and the K_2O of 0.5-1.7%. It appears that there is a possibility of alkali-aggregate reaction to occur for concrete with these aggregates as one of the main constituents.

Figure 3 Pampanga sampling site in 1996, showing the extent of volcanic debris deposited under a bridge with former clearance height of 24 meters.

Table 1
Summary of the physical properties of Pinatubo aggregates from various sources

		Pampanga			Tarlac	Zambales		
Physical Properties	ASTM Method	Pasig-Potrero	Lubao	Mabala-cat	Bamban	San Felipe	Sto. Tomas	Botolan
I. Fine Aggts Specific Gravity	C-128	2.0- 2.3	1-9-2.6	2.3-2.6	2.0-2.4	1.8-2.7	1.9-2.2	1.9-2.1
Absorption (%)	C-128		1.3-4.1	1.7-2.9	1.8-3.1	2.3-3.6	2.1-4.0	1.8-3.0
Fineness Modulus	C-136	1.5- 3.8	3.20	2.74	2.56	3.20	2.65	2.50
Unit Wt. (kg/m³)	C-29	2.74	1497	1390	1290	1190	1298	1190
% fine (0.15-0.075)	C-136	1250	2-16	3-10	4-18	4-15	5-15	4-12
		5-12						
II. Coarse Aggt Specific Gravity	C-567	1.25	1.31	1.25	1.26	1.28	1.22	1.33
Absorption (%)	C-127	25.9	29.0	28.2	30.0	29.0	27.3	24.0
Unit Wt. (kg/m³)	C-29	655	657	660	680	680	675	640
% Coarse/m3 volume	C-136	15-30	20-40	10-25	5-25	15-25	20-40	20-40

Table 2.
Oxide Analysis of Cement and Mineral Admixtures (Pozzolans)

Location	Code	Type	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O
1. Mabalacat	P1	Pumicite Stones	61.7	17.6	4.3	4.3	1.2
	L1	Lahar sand	61.3	18.1	4.6	4.2	1.5
	L2	Lahar sand	64.5	17.4	4.4	4.1	1.5
2. Pasig Potrero	P2	Pumicite stones	62.9	18.1	4.6	4.4	1.5
	P3	Pumicite stones	60.3	18.6	5.8	4.8	0.9
	L3	Lahar sand	63.1	17.9	4.4	4.1	1.4
	S1	Slurry sediments	64.4	18.0	5.0	4.3	1.6
	S2	Slurry sediments	61.3	19.7	6.2	4.7	1.0
3. NPC Bataan	FA	Fly-ash	81.1	15.5	1.0	0.1	0.6
4. Cement	OPC	ASTM Type 1 Portland	21.8	5.1	3.1	0.2	0.4

Table 3.
Physical Properties of Cement and Mineral Admixtures (Pozzolans)

Properties	Pumicite Stones			Volcanic Sands			Volcanic Slurry Sediments		Fly-Ash	Cement
	P1	P2	P3	L1	L2	L3	S1	S2	FA	OPC
1.Specific Gravity	2.40	2.46	2.44	2.44	2.50	2.50	2.40	2.42	2.13	3.12
2. Setting Time Initial (h-min)	1-22	1-12	1-18	1-06	2-10	1-52	1-50	1-46	1-51	1-26
Final (h-min)	3-16	3-20	3-12	3-32	3-26	3-12	3-25	3-18	3-44	3-11
3. Water Requirement (%)	103.8	108.5	104.0	106.5	112.0	103.8	108.0	102.0	98.0	100.0
4. Pozzolanic Index with Cement (%)	87.5	92.3	92.5	85.7	85.5	91.3	107.1	96.4	118.5	100.0

3. POZZOLANIC REACTIVITY WITH CEMENT BASED MATERIALS

Natural types of pozzolans are classified as volcanic/zeolitized glass and pozzolanic tuffs of organic origins. The volcanic ash, and lava deposits ejected by the Mt. Pinatubo can be classified under the volcanic glass grouping (Delos Reyes, 1994). Pyroclastic flow (sandy and pumiceous) deposits was estimated at a volume of 5-7 km^3 during the 1991-1992 volcanic activity. Flow observed from Mt. Pinatubo is differentiated as hyper concentrated stream flows and debris flow. The hyper concentrated flows are dense suspension of sediment in water with sediment content of about 40-60%. Debris flow, on the other hand, appears as liquefied slurry with consistency comparable to wet concrete and with fragments ranging from clay to boulder size. These observations confirmed the nature of Pinatubo ejecta in terms of its geological history and mineralogical properties (see Table 2).

3.1. Pozzolanic index with cement

Pozzolanic activity index test (ASTM C-311) with cement showed that Pinatubo ejecta in the form of slurry sediment (S1, S2) and the pumicite stones (P2, P3) have the highest silica reactivity range of 89-97% comparable to 118% of local coal fired-power plant fly-ash (see Table 3). These values are well above the 75% limit set by the ASTM C-618 specification for natural pozzolan. It is again confirmed in this experiment that the pozzolanic activity index of various type and source of ejecta are widely varied, and indeed there is a need for a faster evaluation of the activity index besides the ASTM C-311 test requirement of 28 days sealed curing (Jorillo, P and Verdejo, B, 1996).

3.2. Response of blended cement mortar under natural curing condition

It was observed that in spite of the varied 28-day strength for the 8 types of ejecta materials, generally the strength of blended cement mortar with pozzolanic addition of up to 20% possessed strength 10-30% higher than that of ordinary portland cement mortar. It can be noted, that even though the Pinatubo debris material came from one source, the reactivity of different samples are widely varied. The authors believe that this may be attributed to the following reasons:

a) Reactive glass originated from various explosive eruptions has varying thermal history and different cooling process, and this greatly influences the degree of reactivity and crystallinity of the ejecta materials.
b) Hyper concentrated flow and debris flow of ejecta material from the volcano allowed the separation of minerals according to size, density and crystal type. The volcanic ejecta flow must have induced the separation of minerals according to its fineness, density, and crystal type, thereby causing the varied pozzolanicity of various lahar materials.

For cement replacement greater than 30%, it can be expected that a marked decrease in strength of as much as 50% will occur at the age of 7 days. This observed trend of slow strength development is a typical characteristic for general pozzolanic materials. Optimum proportion for the Pinatubo pozzolans are quite difficult to judged at 28 days, however, at 63 days it can be seen that 30% cement replacement will produce strength at par with plain cement mortar (Shimizu et.al, 1996).

3.3. Response of cement blended mortar under high pressure steam (Autoclave) curing

Cement replacement of up to 30% seems favorable and gives high strength results. An average increase of 18-25% can be expected for 30% replacement, while an average of 10-15% for 5, 10 and 20% replacement. The difference in the strength increase observed for various percent of pozzolan can be attributed to the total available amount of silica reacting with the $Ca(OH)_2$ of cement. Optimum proportion of cement and Pinatubo pozzolan under autoclave method of curing appears to be 60:40, that is, a replacement of cement by lahar to as high as 40%. Silica reactivity and latent hydraulicity of both Pinatubo pozzolan and the local fly ash can be sufficiently enhanced by elevated high pressure steam curing of 15 kgf/cm^2 for 3 hours. Autoclaving method can therefore be used as an accelerated curing technique in the determination of the degree of pozzolanicity of lahar material and also in the determination of the optimum proportioning of ejecta with Portland cement (Jorillo et.al, 1996).

3.4 Pinatubo as mineral admixture for durability of blended cement-based concrete

In concrete, the general concept in improving durability against aggressive medium is to use chemical and/or mineral admixtures such as natural or artificial pozzolans. The amount required depends on the source and type (physical and chemical properties), and may vary from 10 to 60%. Volcanic ash, lava deposits, active clay, santorin earth and trass are few of the many natural pozzolans which have been in used for over thousand of years in making cementitious products. This paper presents the durability properties of a blended cement mortar with Mt. Pinatubo ejecta as pozzolanic material.

Experimental results from the work of Jorillo et al, (1996) has shown that Mt. Pinatubo ejecta is a highly feasible pozzolanic material for active addition to cement in construction, cement and concrete industries, and significant conclusions drawn are as follows.

1. The drying shrinkage values of the blended pozzolan cement mortar were found to be essentially similar with plain mortar. A 10 and 20% pozzolan content showed a slight increase of 13-25% in shrinkage, while a 40 and 50% pozzolan showed a decrease of about 5-10% in the drying shrinkage.
2. Introduction of pozzolanic material to the cementitious binder significantly improved the resistance of mortar against acid attack. A minimum of 20% pozzolan content can reduce loss in weight and surface deterioration in severe acid environment. This significant improvement can be attributed to the reduction and consumption of $Ca(OH)_2$ by the SiO_2 of the pozzolans, and the formation of new denser types *CSH* that is more resistant to acid attacks. Also, blended cement mortar with Pinatubo pozzolan at minimum content of 20% likewise showed a significant reduction in expansion and loss in weight.
3. ASR expansion can be significantly reduced by the use of Pinatubo blended cement mortar with a pessimum proportion or upper limit of 30% pozzolan content. Pinatubo aggregate showed an innocuous property from the JIS 5308 test method.

4. PINATUBO EJECTA AS AGGREGATE CONSTITUENT TO CONCRETE MATERIALS

At present, there are no sufficient data published on the actual use of Pinatubo volcanic debris materials for structural purposes, i.e., (1) no extensive study on the use of volcanic aggregate as component to structural concrete, (2) no detailed characterization of Pinatubo as lightweight concrete material suitable for structural purposes. This study presents suitable mix design and design tables using the Pinatubo aggregate.

4.1. Materials and Methods

Determination of the physical and mechanical properties of fine aggregates and coarse aggregate (pumicite stone) collected from the site was carried out in accordance to ASTM. Ordinary river sand with specific gravity and absorption of 2.45 and 4.38 respectively and fineness modulus of 3.1 with a unit weight of 1536 kg./cu.m. was used as fine aggregate. The coarse aggregate were graded separately and combined during mixing. Three particle size gradings were adopted in the study, namely Grade A, B and C, referring to their descending degree of coarseness (refer to Table 4). The average specific gravity and absorption of coarse lightweight aggregate are 1.116 and 23.937 respectively with unit weight of 600 kg./cu.m.

Table 4
Particle size distribution of coarse aggregates used in the study

Grading code	Percentage passing sieve size opening				
	25 mm	20mm	12.5mm	10mm	5mm
Grade A	95	65	25	10	2
Grade B	100	10	40	10	5
Grade C	100	100	100	25	10

4.2. Effect of cement content to strengths at age 28-day

Series of trial mixes established base line information of mix quantities and proportion of cements, different types of aggregates, workability conditions needed for the production of structural lightweight concrete. Table 5 gives the detailed mix quantities and fresh properties of Pinatubo lightweight concrete. Cement content range of 200 - 400 kg/cu. m. were able to produce a 28-day strength ranging from 10 - 21 MPa (1500 - 3000 psi) for various types of lightweight aggregate combinations namely all-lightweight, and sand-lightweight.

Figure 4 shows the result of the compressive strength and cement content for all-lightweight concrete, sand-lightweight concrete and semi-lightweight concrete. Generally, the trend shows the normal behavior of concrete strength with respect to the cement content. Based on the figure, variation in strength properties of all-lightweight concrete, sand-lightweight concrete, and semi-lightweight concrete appears minimal. If the trend is compared with the ACI 211.2 bandwidth for structural lightweight concrete, it is apparent that the strength ceiling of Pinatubo lightweight aggregate has been reached at cement content of 450-500 kg/m3. Various mix parameters such as grading, type and combination of fine aggregates, aggregate/cement ratio and cement content have a significant effect to the mix proportions and resulting fresh and hardened properties of lightweight concrete.

a. The compression, tensile and flexural strength, as well as the unit weight, increases in proportion to cement content (Fig.5).
b. The effect of different combination of fine aggregates (e.g. Pinatubo or ordinary river sand) to the mechanical properties can be considered negligible.
c. Grading and volume of coarse aggregate have significantly affected both the fresh and mechanical properties and the mix quantities.
d. Figure 6 shows the relationship of cement content to aggregate/cement ratio of different lightweight aggregate concrete respectively. It can be seen from the figures that the strength decreases as A/C ratio increases.

An increasing volume of lightweight aggregates, V_{aggt} will definitely affect the overall strength of concrete. Higher A/C lead to a relative increase in volume of aggregates compared to cement content, and hence a relative change in the amount of the binding materials compared to the material to be binded. Neville (1981) pointed out that, "the strength of concrete results from (1) the strength of mortar, (2) the load between the mortar and the coarse aggregate, and (3) the strength of the coarse aggregate particle."

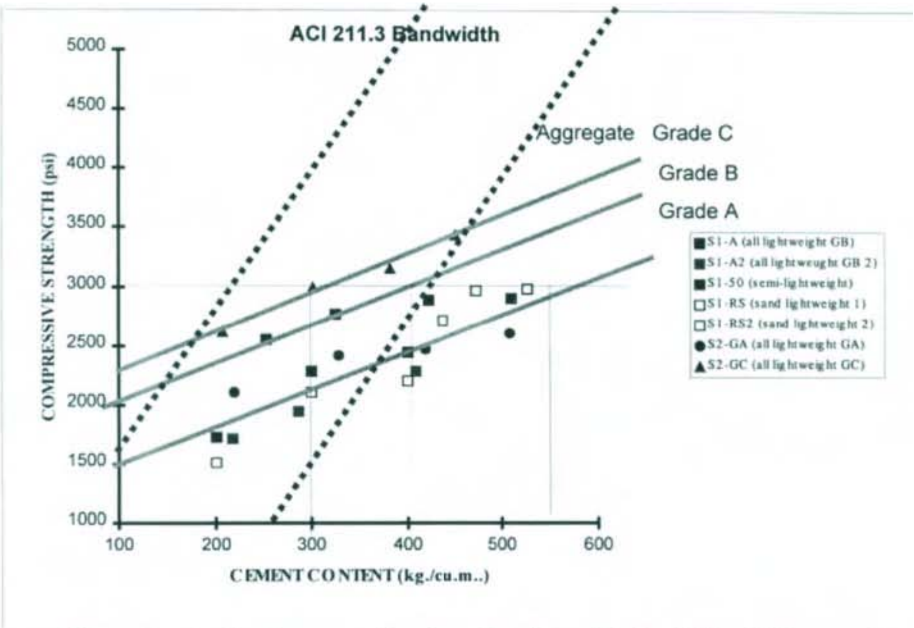

Figure 4 Cement content and compressive strength relationship for lightweight concrete

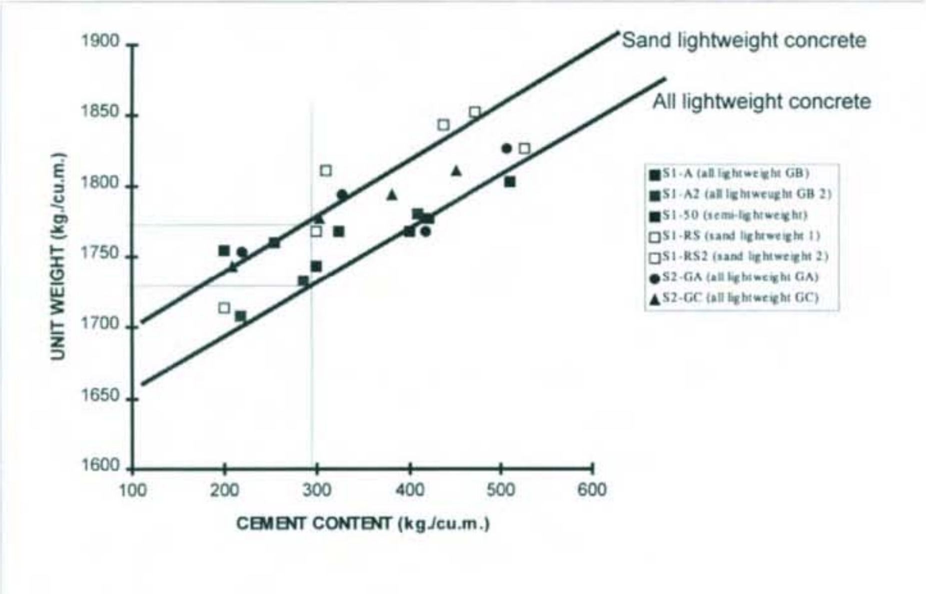

Figure 5 Relationship of cement content to the density of lightweight concrete

The Law of Mixture states that the overall strength of a composite material is a summation of the strength of the constituent materials relative to its volume percentage of the composite (Hannant 1981), i.e.,

$$E_{concrete}\, V_{concrete} = E_{matrix}\, V_{matrix} + E_{aggt}\, V_{aggt} \tag{1}$$

For a unit volume,

$$E_{concrete} / E_{matrix} = 1 - V_{aggt} + (E_{aggt} / E_{matrix}) V_{aggt} \tag{2}$$

Where : E and V refer to elastic modulus and volume fraction respectively.

The suffix $_{concrete}$, $_{matrix}$ and $_{aggt}$ give reference to the concrete composite materials, mortar matrix and the coarse aggregate respectively.

Hence, the strength ceiling of the lightweight concrete is dependent on the volume and strength of the aggregate, as well as that of the matrix. At fixed cement content the volume of aggregates can be suitably decreased to achieve a range of workability of 75 - 150 mm slumps for various application. Also, from the result of the strength tests, it can be seen that the excellent type of grading of aggregates is Grade C. The size distribution of these grading contains an 80% 5-10mm and 20% 10-20mm coarse aggregate. One factor, which affected the strength, is the presence of local stress concentration in the concrete material, which is more significant for large size aggregates.

4.3. Guide Design chart for mix design

Mix proportions of a given concrete material maybe dictated by the following requirements: strength; unit weight; minimum cement content; slump; and maximum size of aggregate.

Establishment of batch weights per unit volume can be executed by the following steps:

Step 1 Estimating Cement Content: ACI 211.2-5 recommended that the aggregate producer or supplier be consulted to obtain closer approximate of the cement content required to achieve desired strength with the specific aggregates. For Pinatubo lightweight aggregate Fig.4 enables the estimation of cement content based on a given target strength. For example, for Fc' of 3,000 psi (21Mpa) and 10 mm maximum size aggregates, the cement content is 300 kg/m3. Likewise, if the criteria for the mix design is the unit weight, Fig.5 enables the initial estimation of the cement content.

Step 2 Choice of maximum size of aggregates and estimation of aggregate volume: Large maximum size aggregate requires less mortar per unit volume of concrete, vis-a-vis, small maximum size aggregate due to larger total surface area which requires more mortar per unit volume. Hence, choice of size of aggregate apart from the construction site requirement determines the total volume of aggregate based on workability requirement. Fig. 6 enables the estimation of the total aggregate for the mix based on the cement content.

Step 3 Estimation of Fine aggregate content: Results of series of trial mixes showed a cohesive and excellent finishability characteristics of Pinatubo lightweight concrete having a sand-aggregate (S/A) ratio of 0.40 to 0.475. Using Figure 7 can make initial estimate.

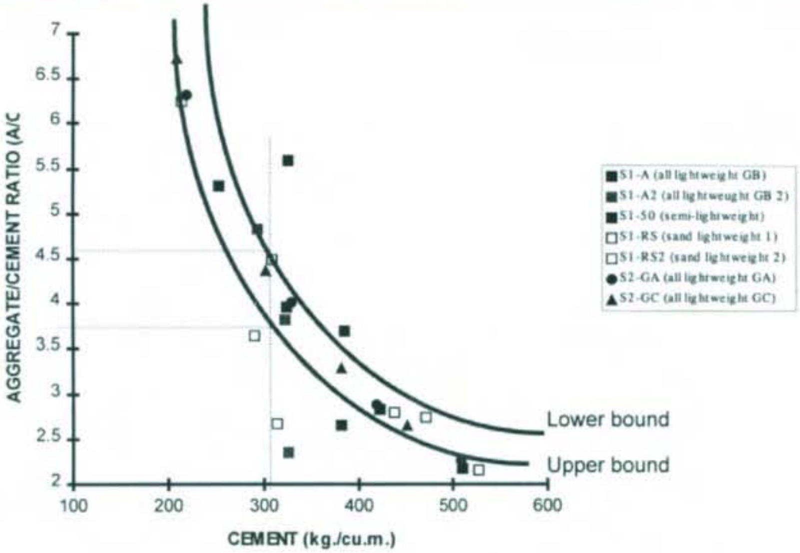

Figure 6 Aggregate-cement ratio and cement content relationship of lightweight concrete

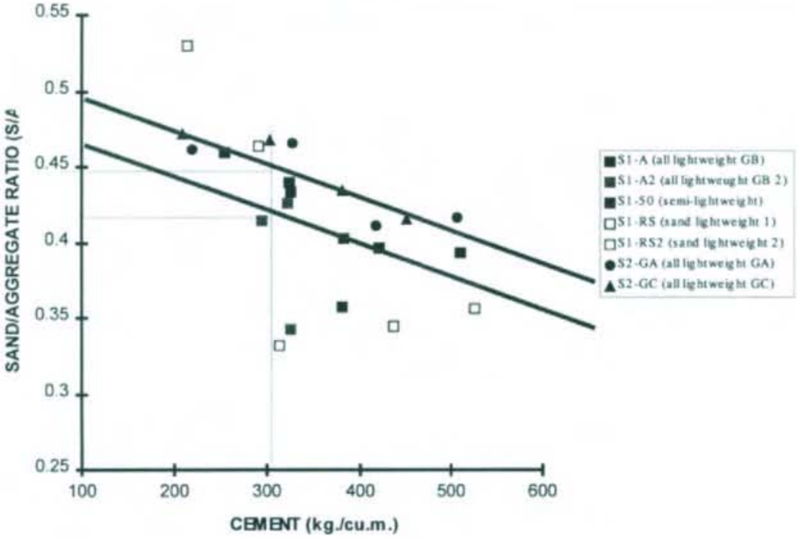

Figure 7 Effect of cement content to the sand requirement of lightweight aggregate concrete to obtain a highly finishable and cohesive mix

Table 5:
Mix quantity and fresh properties of Pinatubo lightweight concrete (all lightweight, sand-lightweight types)

Mix code	Mix Quantities (kg/m^3)										Fresh Properties		
	Binder		Admixture		Water	Fine Aggregates		Coarse Aggregates			Slump	Air	Unit wt
	Cement	Pozz	AEA	WR		Ejecta	River	5-10 mm	10-20	20-25	(mm)	(%)	(kg/m3)
S1-200/All	253	-	0.03	3.80	164	616	-	202	525	-	90	3.3	1760
S1-300/All	324	-	0.05	4.86	160	564	-	179	540	-	110	4.0	1768
S1-400/All	422	-	0.08	6.33	162	472	-	180	541	-	110	1.6	1777
S1-500/All	510	-	0.13	7.65	178	437	-	178	498	-	140	1.9	1803
S1-200/Sand	309	-	0.05	4.64	201	-	409	246	737	-	70	1.1	1811
S1-300/Sand	437	-	0.09	6.55	184	-	421	241	559	-	50	2.6	1844
S1-400/Sand	527	-	0.12	7.91	165	-	406	225	511	-	140	1.8	1827
S1-500/Sand	472	-	0.15	0.07	102	-	629	166	498	-	180	1.6	1853
S2-200/GA	219	-	0.03	3.28	132	639	-	75	428	242	60	1.4	1735
S2-300/GA	328	-	0.07	4.91	148	614	-	68	403	233	110	1.0	1794
S2-400/GA	418	-	0.10	6.27	147	495	-	69	392	248	140	0.9	1768
S2-500/GA	508	-	0.16	7.62	171	478	-	67	368	235	180	1.5	1827
S2-200/GB	253	-	0.03	3.80	164	616	-	202	525	-	90	3.3	1760
S2-300/GB	324	-	0.05	4.86	160	564	-	179	540	-	110	4.0	1768
S2-400/GB	422	-	0.08	6.33	162	472	-	180	541	-	110	1.6	1777
S2-500/GB	510	-	0.13	7.65	178	437	-	178	498	-	140	1.9	1803
S2-200/GC	208	-	0.03	3.11	136	660	-	601	138	-	30	2.4	1743
S2-300/GC	302	-	0.06	4.54	155	618	-	569	133	-	140	3.0	1777
S2-400/GC	382	-	0.09	5.72	155	545	-	522	189	-	150	2.7	1794
S2-500/GC	451	-	0.14	6.76	165	496	-	505	194	-	160	3.2	1811

Notation on the mix code refer to the following: *S* refers to the number series, *200* to *500* refers to cement content, and *GA,GB,GC, All, Sand* refer to the type of aggregate used.

Step 4 Estimation of Water: Applying the absolute volume method of computation - with the initial estimate of (1) cement, (2) aggregate volume, (3) sand, and (4) air-entrainment requirement, the amount of water in a given unit volume can be computed

6. CONCLUSION

This R&D Program has shown that the Mt. Pinatubo ejecta is a significant prime replacement construction materials, which is indigenous, abundant and readily available. Utilization of this material will solve two problems, namely, partial elimination of unwanted materials, and provision for a valuable source of raw material. Significant conclusions draw from the experimental programs are:

1. Chemical, physical, and mineralogical characterization of Pinatubo ejecta enable the identification of its possible applications in the cement, concrete and general construction industry. Pinatubo ejecta is a highly siliceous material rich in aluminum, calcium and sodium with varied pozzolanicity. The pozzolanic activity index varied from 82-97%, and the physical and chemical properties as set by the ASTM C-618 specification for natural pozzolans are within limits. Hydrothermal reactivity of the Pinatubo pozzolan was also confirmed in the study.
2. Pinatubo coarse aggregate is a satisfactory natural lightweight aggregate for structural concrete. Base line relationships and information on mix proportions under different conditions were established.
3. Cement content range of 200 - 400 kg/cu. m. were able to produce 28-day strength ranging from 10 - 21 MPa (1500 - 3000 psi) for various type of lightweight aggregates combinations namely all-lightweight, and sand-lightweight. Design charts derived from this study will enable the prediction of cement content, fine and coarse aggregate proportions, based on either required compression strength, unit weight or workability

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Development of utilization technologies for Mt. Pinatubo ejecta as prime material for concrete: Part 2 – Testing the Structural Performance of Modular Panels

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The Technological University of the Philippines in cooperation with Nihon University, and Japan's Ministry of Education, launched an R&D project on utilization of Mt. Pinatubo ejecta for modular housing construction. One of the major concerns of the Philippine government is how to provide decent and affordable housing units to the Filipino masses. A possible answer to this is to come up with pre-cast and modular structural components that will facilitate speedy and low-cost construction of residential buildings. Another aspect of this study is the utilization of volcanic aggregates from the 1991 Mt. Pinatubo eruption. The utilization of this abundant material will address both the ecological problem and the challenge to create cheaper but quality construction materials.

1. INTRODUCTION

Modular panel is a structural element of predetermined shape and size, cast in a factory for the purpose of mass production and rapid use in construction. Panel elements measuring 500 mm and 1000 mm long would be ideal for wall, slabs, and even for beams. The maximum weight that can be handled by two people was considered in deciding the configuration of the panel. Design was based on the National Structural Building Code of the Philippines (NSCP). The size of the panel is intended for the construction of 3m x 3m room units as designed by Tsuboyama et al (1998). Reinforcement was arbitrarily selected so that the calculated structural capacity of the panel will satisfy the expected loads based on the stipulated loadings in the NSCP.

The objective of this research project is to provide an experimental and analytical characterization of Pinatubo ejecta material for modular housing applications. This paper forms the second part of the study.

2. EXPERIMENTAL PROGRAM

2.1. Materials and Methods

Determination of the physical and mechanical properties of fine aggregates and coarse aggregate (pumice stone) collected from the site was carried out in accordance to ASTM. Ordinary river sand with specific gravity of 2.45, absorption of 4.38, fineness modulus of 3.1, and a unit weight of 1536 kg./cu.m., was used as fine aggregate. The coarse aggregate were graded separately and combined during mixing. The three gradings adopted in the study are Grade A, B and C, with descending degree of coarseness with optimum packed density as previously designed by Jorillo (1997). The average specific gravity and absorption of coarse lightweight aggregate are 1.116 and 23.937 respectively with unit weight of 600 kg./cu.m (refer to Part 1).

The panel highlights the use of structural lightweight concrete made of Mt. Pinatubo aggregates. The 28-day compressive strength of concrete is 20.7 MPa while the unit weight is 1817 kg/m^3 (Shimizu et al, 1992). The main reinforcement used are the locally available grade 40 (fy=40 ksi or 275 MPa) 10 mm□□ deformed steel bars. Actual test of steel however indicates higher yield strength of 316.6 MPa. In addition, wire mesh with yield strength of 705 MPa was used as supplementary reinforcement.

2.2. Panel specimen

There were two configurations of wall panel specimen examined in the program. The size of the panel is intended for the construction of 3m x 3m room units, either for one-storey or two-storey houses. The shape is so designed to make the weight as light as possible. Reinforcements were arbitrarily selected so that the calculated structural capacity of the panel will satisfy the expected external loads based on the provisions stipulated in the NSCP (Lejano et al, 1998).

1. A panel with 40 mm thickness surrounded by a rib measuring 50 mm wide by 100 mm thickness was prepared. The reinforcement and specimen configuration are shown in Fig. 1. Tests were conducted both at the laboratories in Nihon University, Japan and at the Technological University of the Philippines as part of University-University joint research program.
2. A flat panel of dimension 50 x 600 x 2400 mm for flexure and 50 x 600 x 600 mm for compression test per ASTM E- 72 Sec. 9 and 11 were also prepared. Tests were conducted at the Technological University of the Philippines as part of the Department of Science and Technology-Philippine Council for Industry and Energy Research and Development grant-in-aid project.

2.3. Mechanical property test of wall panel

The mechanical properties were characterized in terms of first crack load, ultimate load, load-deflection behavior, and stress-strain response during loading, and cracking behavior. The load-deflection diagram provides a complete loading history response of the pre-cast wall element and information regarding the elastic characteristics (first crack), post-cracking behavior, ductility and toughness. Observations of deformation response are grouped in first crack and post-crack stages. Elastic stage covers the linear response of stress and strain or load-deformation curves, after which micro-cracks progress in the direction of the principal strain causing stiffness reduction and non-linear behavior, this is known as the post-crack stage.

1. For ribbed panel, three set-ups were conceived to evaluate actual strength (see Figs. 1 to 3). Setup A simulates the slab or wall with the load acting towards the structure (positive bending), setup B is the reversal loading of setup A (negative bending), and setup C is a shear flexure beam test.
2. For flat panel, ASTM E- 72 Sec 11 *Conducting Strength Tests of Panels for Building Construction* was adopted (see Fig. 1). Flexural test were done using four-point load with load-deformation measuring system attached to the wall panel. Corresponding strain was measured using strain gage at strategic locations, and connected to the data logger for the simultaneous measurement of stress and strain.

3. RESULTS AND DISCUSSION

3.1. Test results of ribbed lightweight wall panel

Listed in Table 1 are the salient information about the panels and the corresponding test results. Also tabulated is the comparison between M_{exp}, M_{calc}, and M_{load}, where M_{exp}= 90% of the max. moment obtained from test, M_{calc}= ultimate moment (90% of nominal moment) based on NSCP, and M_{load}= max. external design moment for different factored load combinations based on NSCP specifications. Calculation was done assuming singly reinforced section. In general, the tested panels are adequate for the design loads as manifested by $M_{exp}/M_{load}>1$.

Table 1
Summary of panel data and test results

Panel No.	Wire Mesh	Test Setup	Conc. Age	fc' (MPa)	P_{max} (tf)	M_{exp} (N-m)	M_{calc} (N-m)	M_{exp}/M_{calc}	M_{load} (N-m)	M_{exp}/M_{load}
1	5 mm	A	28	20.7	3.544	4689	2931	1.60	3011	1.56
2	5 mm	B	28	20.7	2.700	3572	2533	1.41	2007	1.78
3	5 mm	C	28	20.7	6.830	11295	9287	1.22	5696	1.98
4	3 mm	C	28	20.7	6.454	10673	9287	1.15	5696	1.87
5	5 mm	A	12	17.7*	2.099	2777	2914	0.95	3011	0.92
6	5 mm	B	19	19.4*	2.420	3202	2498	1.28	2007	1.59
7	3 mm	A	14	18.3*	2.502	3310	2918	1.13	3011	1.10
8	3 mm	B	28	20.7	2.232	2953	1261	2.34	2007	1.47

Significant characteristics observed are as follows.

1. In Fig. 4 the load-deflection relationships are shown. Generally, ductile behavior is observed for panels under the positive bending (set-up A) while relatively brittle behavior when under negative bending (set-up B). When set C was adopted, smaller midspan displacement is observed. Furthermore, under set-up C, panel with smaller wire mesh diameter exhibits more brittleness.
2. Flexural and shear cracks were observed on the panels. These cracks were mainly visible on the rib of the panel indicating that the damage rib initiated the failure (Fig.3).

3. Tested panels are adequate for the design loads as manifested by $M_{exp}/M_{load}>1$. Even for panels, which have, weaker concrete exhibited satisfactory M_{exp}.

Although panels with 5 mm wire mesh diameter showed higher M_{exp} than those with 3 mm diameter, it might be concluded that the 3 mm wire mesh is more than adequate.

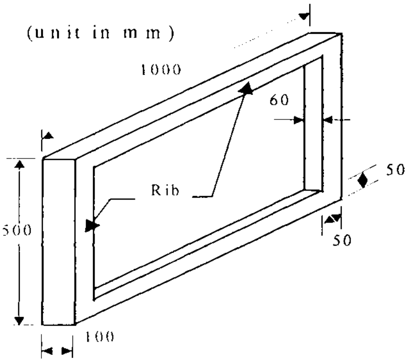

Figure 1 Cross-section of the ribbed slab

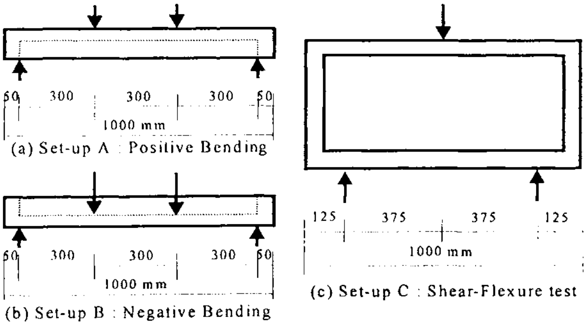

Figure 2 Configuration of different test set-up for the ribbed panel

Figure 3 Flexural test setup of the ribbed panel

5.4. Test results of flat lightweight wall panel

1. A higher designed matrix strength (e.g. Class A= 20.5 MPa) resulted in a higher range of flexural first crack strength (3.5-4.0 MPa or 350-475 psi). It is at this elastic stage that Hooke's law is valid and resisting moment capacity of the wall element depends on the concrete properties

2. In spite of drop of load after the occurrence of first major cracks, the handling reinforcement was able to maintain the strength capacity of wall element even at very large deformation. This indicate the capability of the wire mesh reinforcement to control the opening of the crack, enabling partial redistribution of stresses to occur at portions which are least stressed.
3. Wire mesh is customarily used to provide some form of secondary reinforcement in the form of handling, overloading, impact or shrinkage reinforcement (Fig.5). In this case, results showed that the wire mesh was able to retain the structural integrity of the wall element after cracking, and in many instances acted as primary reinforcement that enable the wall element to carry up to 200% of the first crack load. It can be observed in that in some instances along the diagram abrupt decrease in loads occurred. This may be due to bond slippage between the concrete and the wire mesh. S1-200 with Fc'= 12 Mpa or 1500 psi when compared with S1-400 series with Fc'= 20.5 MPa or 3000 psi will show a bond slippage (or abrupt decrease in load due to crack propagation) occurrence of higher frequency (see Figs.7 and 8).
4. Due to the limitation of the deflection measurement system, maximum midspan deflection was recorded up to 25 mm only. Although, continuous increase in both load capacity and deflection was observed for all wall element. High toughness characterized by a pseudo elastic-plastic load-deformation curve was seen in all of the wall panel elements. Multi-cracking due to stress distribution along with the yielding of the reinforcement brought about this kind of characteristic. Structural integrity was maintained even at mid span deformation relative to span ratio of 1/100 to 3/100.

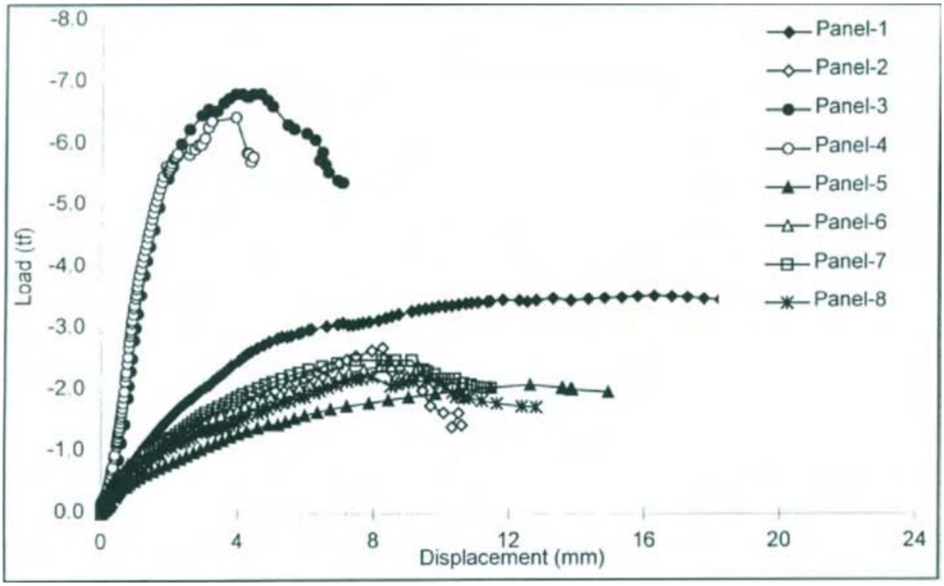

Figure 4: Load displacement relationships of different test set-up of ribbed panel

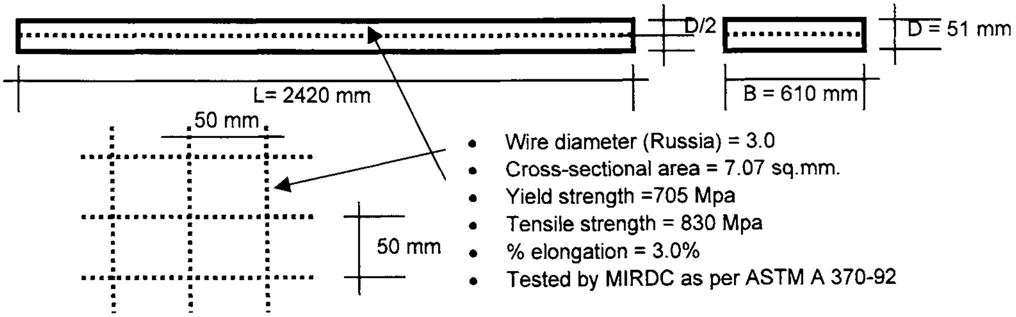

Figure 5. Schematic configuration of 2"x2'x8' flat wall panel element and welded wire mesh reinforcement

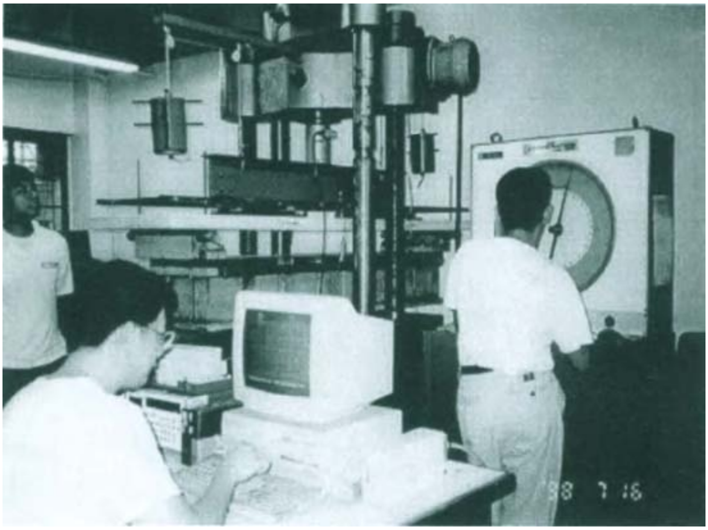

Figure 6 Flat panel flexure test of 50x600x2400 mm specimen

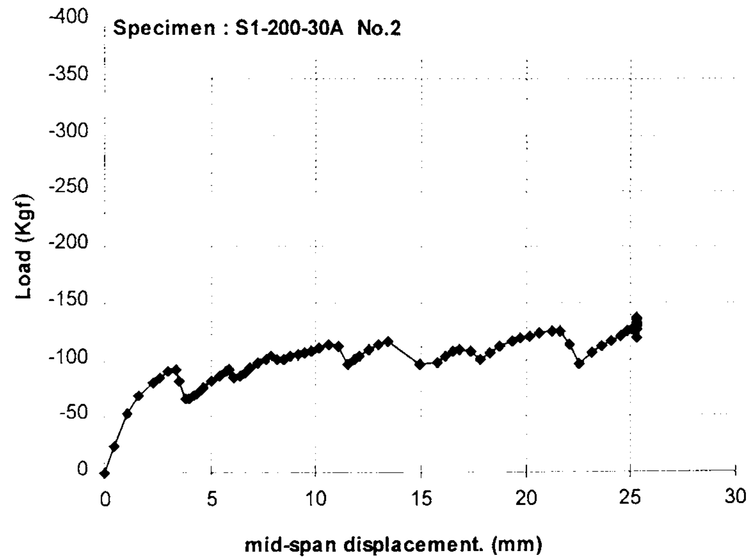

Figure 7 Load-deflection diagram of Class C (Fc'=12 Mpa) flat lightweight panel

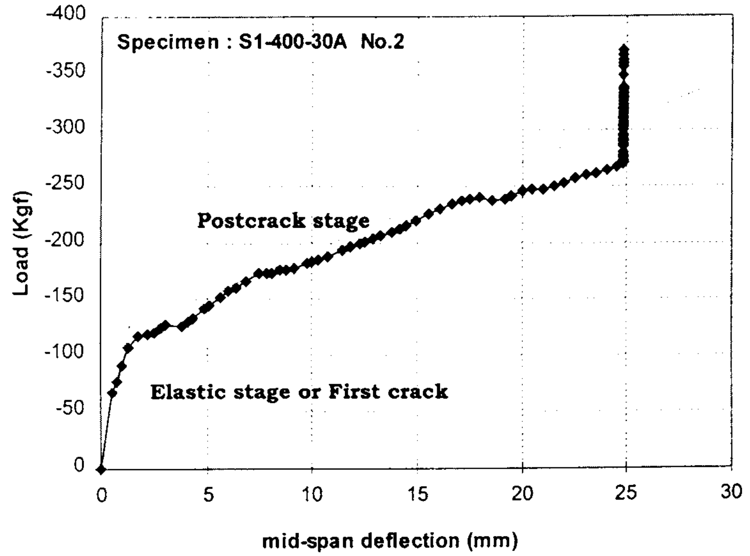

Figure 8 Load-deflection diagram of Class A (Fc'=20.5 MPa) flat panel

6. CONCLUSION

A modular panel that can be handled by two people is presented in this R&D Project. Test results indicate the structural adequacy of the panel both ribbed-type and the flat-type.

Although the 5 mm wire mesh increases the strength of the panel, the 3 mm wire mesh is more than sufficient for its intended structural application.

Prefabrication process of lightweight wall elements or panels has large potential for the future. It is in the direction of high quality products with energy savings and value-added properties in design and installation. The choice of applications in the building and construction industry in the form of cladding panels, modular housing components, panels, sheeting, etc are wide and of tremendous significance. The concrete industry is ideally placed to accommodate and apply the results of this study, using available technologies and strict quality controls. High performance products using indigenous or local materials with emerging technologies are a challenge, for knowledge and experience are scarce. The results of the study provides both knowledge and experience for this particular challenge. The finding in this study is an important step in the advancement of the development of pre-cast products and elements using Pinatubo materials. The viability of the results and the experience learned and gained may serve as take-off points for further development of this material for the general construction industry.

7. RECOMMENDATIONS

The following are recommended action plans for future studies and application of the results of the study.

7.1 Mature technologies for transfer / Dissemination to end-users

- To disseminate the results of the properties of Pinatubo Lightweight concrete to small and medium scale aggregate entrepreneur to boost utilization and acceptance of this type of aggregate, and thus contribute to the betterment of the socio-economic condition of the people devastated by the debris flow.
- To disseminate results of properties of Pinatubo lightweight wall panel to the general construction and concrete industry in order to serve as baseline information in the development of structural elements such as cladding and wall panels.

7.2 Technologies that need further verification

- Pinatubo fine and coarse aggregate is a satisfactory aggregate for concrete mixes. It is recommended that other long-term effects like alkali-silica reaction (ASR) and in-situ degradation be studied.
- Pinatubo pumice aggregates in concrete mixes based on the test results of a limited-range-variable experiment showed a strength capacity of about 24 MPa. Further investigations on its feasibility as a material for high strength structural lightweight concrete is recommended.
- Pinatubo lightweight panel test results showed structural properties recommendable for pre-cast elements in the form of cladding panels and structural wall elements. Mesh reinforcement layout and configuration was not given considerable attention in the study since the object was the characterization of the concrete material itself. Hence, it is recommended that this area be likewise investigated.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

New technology approach to age-old waste material (natural fibers) for composites

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Natural fibers like sisal, hemp, and coir fibers are abundant in many developing countries. Fiber composite cladding panels, prefabricated elements, special tiles and panels are few of the many possible applications of natural fiber cement composites. Socio-economic opportunities involved in the utilization of natural fibers include (1) elimination of solid waste, (2) environment friendly method of disposal, and (3) provision of a viable source of raw material. An R&D project was developed in collaboration with Nihon University, Shimizu Corporation-Institute of Technology, and the Technological University of the Philippines on centrifuged method of casting approach on natural fibers composites for pre-fabricated construction. The study tackled material optimization, and design and test of pre-cast elements using this technique. The paper describes the significant results of the project in the following areas

1. Applications of natural fiber reinforcement in gypsum-based lightweight panel
2. Applications in centrifuged method of casting for pipes and thin walled box sections
3. Application of centrifuged methods for production of gypsum based panels
4. Durability characterization of the natural fiber composites

1. INTRODUCTION

The interest in the use of natural fibers such as sisal (*Agave sisalana*) and coir (*Cocos nucifera linn*) fibers in cement matrices is of more recent origin although the principle of application has been known thousands of years ago. Natural fibers composites have special relevance to developing countries considering their ready availability, savings in energy and their potential applications to the rapid development of a country's infrastructure. The potential for natural fiber cement composite is significant. Agopyan (1990), and Gram (1980) presented some applications of natural fiber cement composites as sheetings, corrugated roofing and pre-cast building components. Socio-economic opportunities in the utilization of this natural fibers for cement-based composites include:

1. Labor-intensive preparation of fibers for mass production of composite elements
2. Environment friendly method of disposal of solid waste such as coconut husk, and
3. Viable source of raw material for the construction industry

Fiber reinforced composite is essentially made from a hydraulic cementitious material (e.g. Portland cement, lime or gypsum binder) with aggregates, and in the main discrete fiber reinforcement (ACI 544). The concept of addition of fibers into a brittle matrix is an attempt to delay of tensile cracking, improvement of tensile/flexural strength, rheological characteristics, ductility provision through post-cracking strength, improvement of toughness, and resistance to impact. However, the degree and effectiveness of reinforcement depends on the type of fiber. Generally high modulus fiber such as glass or steel are capable of producing strong composites. On the other hand, low modulus fibers such as polypropylene and natural fibers are capable of producing composites with high ductility and toughness with moderate increase in strength. Previous works of the authors have shown that natural fibers have many inherent weaknesses such as low elastic modulus, high water absorption, and lack of durability in an alkaline medium, which makes its wide acceptance and use limited (Jorillo et al, 1997). They also noted that the slow development of natural fiber cement composites is due to lack of information on the properties of composites with natural fibers using new technologies. This paper provides characterization of a natural fiber composite in terms of material optimization, design and test of pre-cast elements using emerging techniques for improved structural performance. To establish baseline information on the results of the study, a comparative study was done with synthetic types of low modulus fibers like polyvinyl alcohol (PVA), and polypropylene fibers.

The paper describes the following highlights in the test of

1. Gypsum-based thin wall panel composite
2. Centrifuged (spun) fiber cement composite thin pipes
3. Centrifuged (spun) fiber cement composite thin walled box section for formworks
4. Durability characterizations

2. NATURAL FIBER AS REINFORCING MATERIAL FOR GYPSUM-BASED MATERIAL

Gypsum is obtained by calcining raw gypsum ($CaSO_4.2H_2O$) at around 175°C, and if water is added the resulting hemi hydrate (□-gypsum, □-gypsum) rehydrates back to the di-hydrate form in about 20-30 minutes (Evans et al, 1980). Currently, □-hemi hydrate gypsum is more commonly used in building construction in the form of pre-cast elements because of its slower setting time rate and lower cost compared to □-gypsum, but it is relatively low-strength. In this study, the feasibility of using □-hemi hydrate gypsum as the binding medium for building elements was investigated. The lightweight and fire resisting property of gypsum cement plaster makes it very suitable for panel elements in building construction (Joshi et al, 1992). The low alkalinity of gypsum compared to Portland cement makes it an advantageous cementing materials for natural fiber cement composites where alkali attack on cellulose components of fibers is critical (Neville, 1981).

2.1. Materials and Methods

An α-gypsum (α-$CaSO_4+1/2H_2O$) was used as binder. A crushed sand with maximum size of 3.0mm, specific gravity of 2.45 and absorption of 1.4% was used as fine aggregate. For fiber reinforcement, two general type of low density fibers were used, namely, polymer based fibers with specific gravity of 0.98 to 1.3 (i.e., polyvinyl alcohol or PVA and polypropylene), and natural fibers (see Figs. 1 and 2) with specific gravity of 1.0 –1.15 (i.e., coconut and sisal fibers). Properties of fiber used are shown in the Table 1. The base matrix (i.e. composite without the fibers) has a designed workability of 200 mm slump and was mixed per ASTM procedure. Slight modification of the procedure was made to accommodate the introduction of the fibers into the matrix system, as described by Jorillo et al (1994). Workability in terms of stability, mobility was measured by slump test and the inverted slump test (ASTM C-995). Specimens were cast with an applied pressure of 5 kgf/cm^2, and then moist-cured for 28 days. A casting pressure was hydraulically applied to fresh panel specimen to simulate the pre-cast production of gypsum boards. A 20x150x300 mm and 20x300x600 mm panel specimen were tested per set-up specification of JIS A-1408. Properties in compression, and flexure were taken based on JCI-SF5 (JCI,1984). Simultaneous measurement of mid-strain, mid-deflection and load was also taken to evaluate the entire loading response of the element.

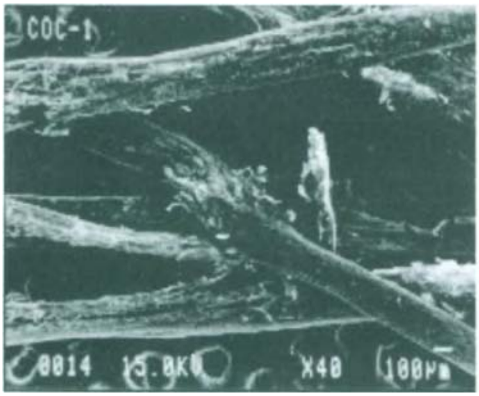

Figure 1. Coir fiber surface morphology

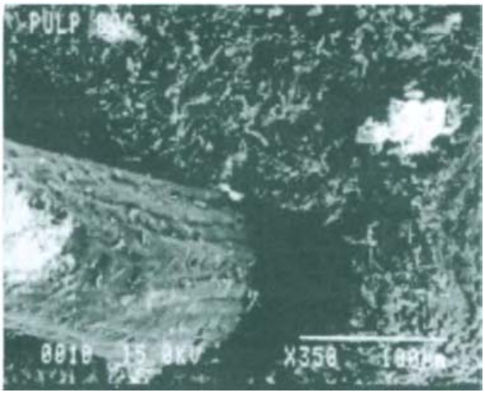

Figure 2. Coir fiber and gypsum matrix interface

Table 1
Properties of reinforcing fibers

Fiber type	Diameter (mm)	Length (mm)	Density (kg/cm3)	Modulus (Gpa)	Tensile (MPa)	Elongation (%)
Vinylon (PVA)	0.2-0.25	12	1300	31	900	6-8
Polypropylene	0.1-0.15	8	910	12	500	8-10
Glas	0.10-0.15	10	2700	70	1250	3-5
Coconut	0.2-0.45	12	1180	8-12	100-150	20-25
Sisal	0.05-0.2	12	1270	12-15	400-460	13-12

2.2. Test results of panel

The objective of the study is to fabricate lightweight, low-cost but of sufficient mechanical strength building element, therefore it was necessary to adopt a high aggregate proportion at relatively lower water-binder ratios (W/B). Based from the experimental results, the following significant properties of the wall panel are drawn.

1. Increasing the lightweight aggregate volume can considerably decrease the flowability of the gypsum matrix. Results showed that a highly flowable but relatively strong gypsum matrix with water-binder ratio (W/B) of 0.35 to 0.45, and aggregate-binder ratio (A/B) of 0.10 to 0.20 can accommodate a fiber volume reinforcement of up to 2%.
2. The gypsum matrix with either paper pulp or artificial ceramics lightweight aggregate follows the same linear binder ratio to strength relationship in the same manner as the cement-based composites. Typical compressive strength of 15-20 MPa, bending strength of 5-6 MPa can have a dry density of about 1500 kg/m^3.
3. Fiber reinforcement to gypsum-based matrix showed a very positive results compared to cement-based matrix. Increase in 7-day flexural strength by 15-25% due to either polyvinyl-alcohol, polypropylene, sisal and coir fiber reinforcement occurred. This characteristics may be due to the relatively low elastic modulus, flexural strength, and ductile property of the gypsum matrix, hence giving the fiber an adequate chance to transfer and redistribute stresses throughout the matrix system. This characteristics is different to that observed in cement matrix were increase in first crack strength even with high modulus fiber like steel and glass were limited to about 15% (ACI 544, 1989).
4. In terms of ductility and toughness, gypsum matrices reinforced with polyvinyl-alcohol (or called vinylon) and sisal showed an excellent load-deformation behavior, followed by the polypropylene and coconut fiber. As the fiber volume increases from 2 to 3%, pseudo-plastic load-deformation characteristics can be observed (see Fig. 4). As expected, the relatively strong PVA vinylon and natural sisal fiber showed an excellent post-crack characteristics. The polypropylene and coir fiber, on the other hand showed only a fair ductile characteristics. It is inferred in this experiment that there is a significant effect to the post cracking strength of the composites the degree of fiber-matrix bonding (refer to Fig.2) and the aspect ratio (l/d).

3. CENTRIFUGED (SPUN) FIBER REINFORCED CEMENT COMPOSITE

Centrifuged or spun fiber cement composite refers to a composite materials cast using centrifugal force at large acceleration of 20-30g, which is achieved through high speed spinning. The combined vibratory and centrifuge action forced the heavier particles to move outward while the lighter aggregate and some of the water are separated and left behind at the inner section, thereby causing a partial segregation of the constituent materials that lead to a non-uniform property along the thickness. However, this segregation and particle movements also produces an advantageous lower water cement ratio and lower porosity characteristics, thereby resulting in higher strength properties. Likewise, for fiber concrete this spinning action tends to re-distribute and re-orient the fibers, depending on their relative densities and aspect ration (l/d), and hence altering the overall quality of concrete materials as well as the property of the whole structural section.

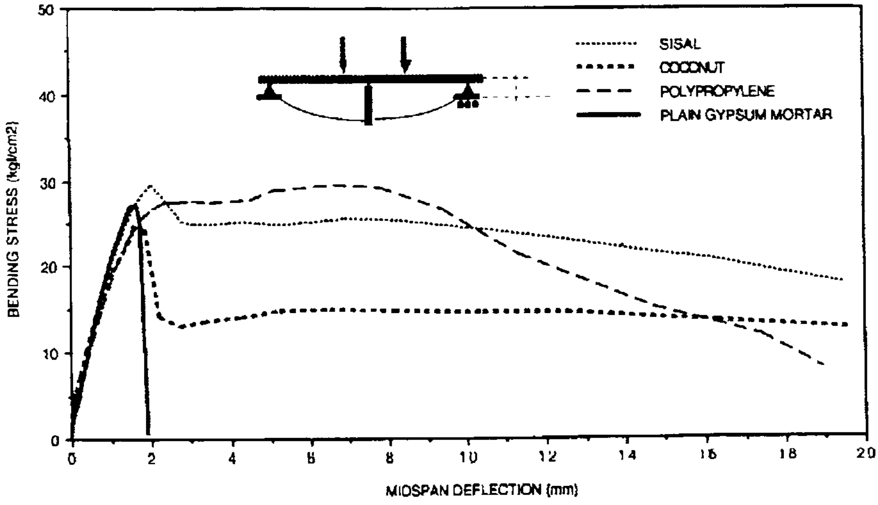

Figure 3 Load-deformation curves of different types of fiber gypsum 20x300x600 panel at fiber volume fraction of 2 %

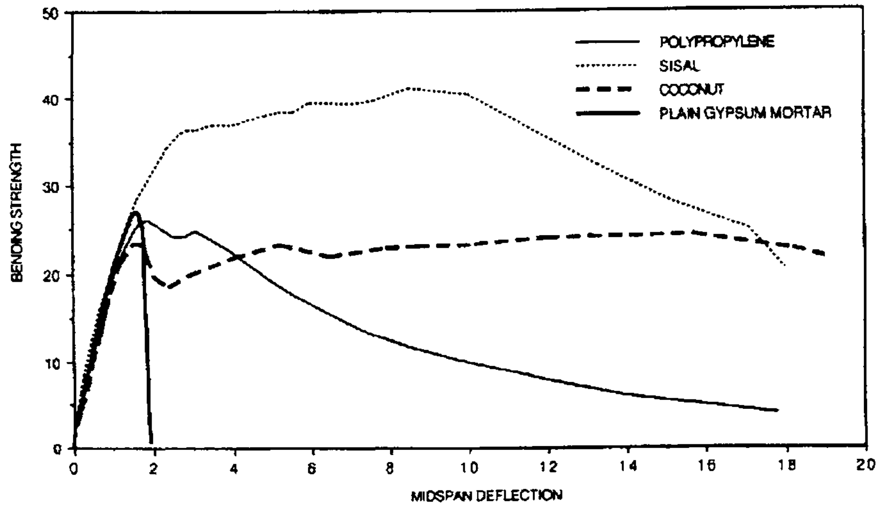

Figure 4 Load-deformation curves of different types of fiber gypsum 20x300x600 panel at fiber volume fraction of 3 %

3.1. Spun pipe section

Materials described in the lightweight gypsum based panel are likewise used in this experimental series. A thin walled pipe section (diameter = 470mm, thickness = 32-34mm, length = 500mm) was cast using centrifugal action. Pipe test under concentrated two-point load was carried out. Displacement of crown towards the invert and horizontal displacement of the springing were measured by a 50 mm transducers (JIS A-1138, 1106, 1108, 1114). Strain gages were place at selected locations to examine the local point stress-strain response of the pipe section. A pipe under external loading is basically an indeterminate structure, the distribution of moment, shear, axial force around the pipe section depends on the variation of bending, shear and axial stiffness of the pipe. The behavior of pipe changes at different stages in its loading history as cracks develop. Fig. 9 show the distribution of moments, shear and axial forces at first crack.

Figure 5. Centrifuge method of casting for test specimen with diameter of 470mm and length of 500mm

Figure 6. Even distribution of coir fibers in the 32 mm thickness pipe

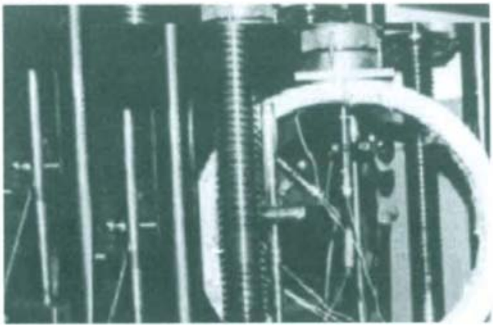

Figure 7. Pipe test set-up, and placement of gages and transducers

Figure 8. Distribution of fibers after centrifuge casting.

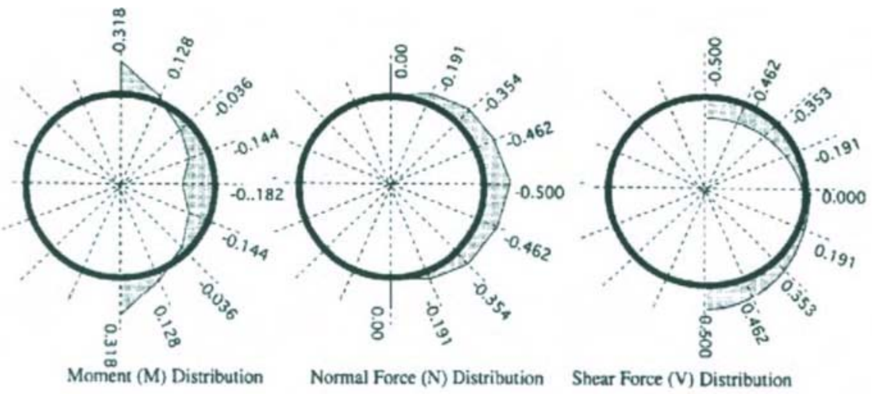

Figure 9. Distribution of moments, shear, and axial forces at first crack stage.

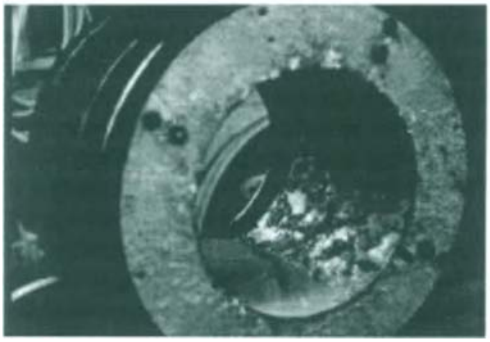

Figure 10. Spun fiber concrete exhibiting severe fiber segregation

Figure 11. Sisal fiber distribution at the inner surface of the spun pipe

3.2. Test result of spun fiber reinforced cement-based composite

1. During centrifugal casting, it was observed that about 48% of the mixing water segregated from the actual mix proportion, and therefore altering the original W/C for 30% to about 14.5% (see Fig.10).
2. It is necessary to optimize the spinning regimen or centrifugal casting that will lead to dense concrete with minimal fiber segregation. Most favorable spinning condition (i.e., time and speed) is dependent on mixture proportions and dimensions of the specimen. It is recommended that this be investigated prior to final test specimen production.
3. It was observed that the compressive strength, Fc', first crack bending strength, Fb, and the elastic modulus, Ec of the this type of fiber composite has increased by an average of 41%, 33%, and 19%, respectively compared to a non-spun fiber composite. This behavior can be attributed to the vibratory and centrifugal action during spinning which efficiently compacted the cement matrix resulting to a less air voids and a more solid and compacted

concrete. Decrease of W/C values from 0.30 to 0.145 is likewise one of the cause of this improvement in strength properties.

4. When the fiber is acted upon by both components of inertial force, the tendency of the fibers to be displaced and re-oriented depends on the density of the fiber, radius from the axis of rotation, speed and acceleration of rotation. Fig. 8 shows the orientation of the coconut fibers at the fractured surface of matrix. It can be observed that all the fibers are more or less reoriented in the direction parallel to the circumference of the pipe section. Both the glass and vinylon fiber showed an increase 2-D reorientation from among the fibers tested. This may be due to its higher density compared to other fibers such as the natural and polypropylene fibers
5. Since the pipe tested in the study are basically unreinforced, it is expected that failure will occur and governed by cracking at four local points, namely, crown, invert and springing, which is a flexural failure type. The mechanism of failure and stages of cracking are clearly shown by the load-deformation test result of different types of pipes. Note that occurrence of cracks is usually accompanied by a drop in load, any increase in load after cracking can be attributed to the ductility of the matrix and the reinforcement of fibers through fiber pullout (see Fig. 8).
6. After first crack strength, the fiber reinforcement enable the pipe to recover and attain a post-cracking strength, which is 20-30% higher. This indicate the capability of the fiber reinforcement to control opening of the cracks, enabling redistribution of stresses to locations, which are least stressed.
7. Load-deflection characteristics of coconut fiber concrete pipe and the polypropylene fiber are basically the same. Generally, for purposes where structural integrity is required against overloading, or accidental impact or handling purposes, these types of fibers would be adequate reinforcement.

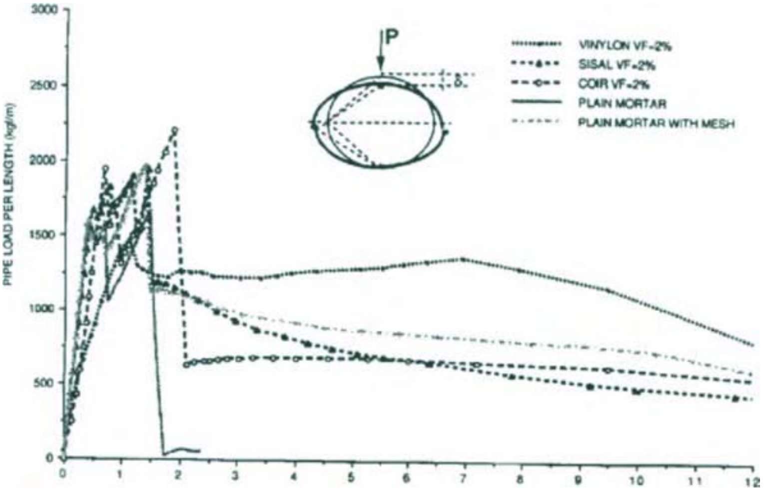

Figure 12. Load deformation diagram of centrifuge cast pipe in comparison with plain mortar pipes with and without #2 wire mesh reinforcement

3.3. Test results of thin walled box section

The thin walled box section has a dimension configuration of 370 mm width, 500 mm length, and 12-15 mm thickness. The box section was cast using additional attachments to the centrifugal casting pipe machine. The box section was cut in half (depth=370, width=185 mm) to produce the C-section. Horizontal and vertical deflections as well as local strains at selected locations of sections were measured simultaneously with the applied load to evaluate the loading response (JIS A-1106, 1108, 1114, 1138). A two-point cantilever-bearing test on C-section was adopted in this study to determine the strength property of a box section (Fig. 13). This loading condition was used to simplify the testing set-up, and this type of loading produces a moment distribution which can approximate the moment distribution of a box section subjected to internal pressure such as newly poured concrete. The application of the thin walled box section is intended as a pre-cast formwork for columns using the loss-of-formwork scheme.

Results showed that in among the test series, the polypropylene fiber showed the best ductility characteristics, i.e., a quasi-plastic load-deformation curve. This behavior can be attributed to the smaller length and higher surface area and aspect ratio of the fiber, which enabled it to be uniformly distributed over the entire thin 12 mm thickness even under the centrifugal action

Vinylon fiber composite showed the highest strength gain among the series but of low ductility. Presence of fiber in such thin section expectedly reinforced the section, however due to the high tendency of vinylon fiber to segregate this resulted to less post-cracking strength.

The other natural fibers showed mediocre results in terms of load-deformation characteristics for this configuration of centrifuged pre-cast element. They exhibited very little strength improvement after first crack, and did not significantly exhibit a plastic behavior. It is presumed that the square configuration of the element, the narrow 12mm thickness, and low fiber aspect ratio under centrifugal action inhibited the uniform distribution of fibers throughout the section.

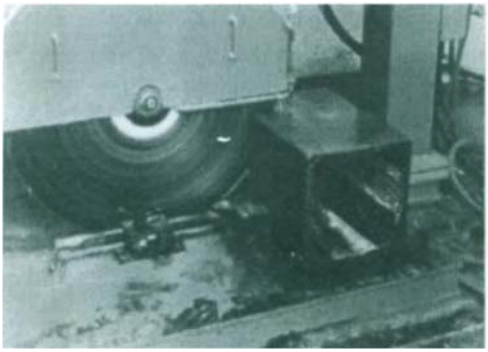

Figure 13(a) Cutting of thin walled box section

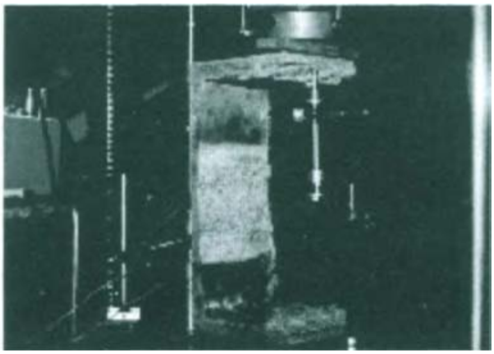

Figure 13 (b) C-type test for the thin-walled box section

3.4. Gypsum Wall panel formed by centrifuged method of casting

Centrifugal method of casting is an effective method of obtaining a high strength material with low porosity and compact structure. It is expected that this type of materials would be more impervious to water and air, and at the same time with added resistance to weathering. This type of method of casting is being used in Japan in the production of artificial but natural looking marble for finished exterior panel and flooring.

In this study, a preliminary test program was carried out to determine the properties of a gypsum-based fiber cement composite tile using the centrifuged method of casting. A polypropylene and coconut fiber concrete mix was cast in the spinning mold, and after centrifuged casting the specimen were immediately demolded and steam cured for 12 hours. After curing, the panel were cut to 150 x 300 mm tile size, and tested at four-point loading.

1. It was observed that aside from the increase in strength, a highly ductile characteristics was seen compared to the same mixture cast using the traditional method of hydraulic press casting for wall panel. Comparison of the load-deformation curve with ordinary casting technique showed higher first crack strength.
2. At present, this type of casting method showed no appreciable increase in the cost-performance of the tile and panel section. However, durability consideration in the future may be one of the added value of this method to a product tile material. It can be concluded from this preliminary work that it is both technically and economically feasible to use this method of casting for pre-cast elements for special applications.

4. LONG TERM PERFORMANCE AND DURABILITY OF NATURAL FIBER COMPOSITE

Visual examination of the fractured surface of a 3-year old specimen cured in natural tropical environment showed uncrystallized fiber characteristics, i.e., fiber brittlement is not yet evident. Shimizu et al (1992) reported that embrittled fiber can lose as much as 20% of the tensile strength with a corresponding increase in bond strength due to increase deposition of hydration products in the lumen of the cellulose fibers. It was also observed from the fractured specimen that the fiber mode of failure is fiber pullout and not by fiber fracture as a result of fiber embrittlement.

Jorillo and Shimizu et al (1992) reported the mechanical property test of specimen exposed to 2000 hours of accelerated weathering (JIS B-7753-77). Weathered specimen showed a significant decrease in post-cracking and toughness with an increase in ultimate flexural strength. It is presumed that the decrease in post-crack strength is due to the loss of fiber reinforcing efficiency due to embrittlement. While the increase in flexure strength is attributed to the normal aging and continued hydration of the cement binder. It is inferred in this test results that the reality of the loss of reinforcing efficiency of the natural fiber with time. Reduction in impact strength as a result of fiber embrittlement was likewise observed. Decrease in impact strength by as much as 60% was observed. Hence, loss of reinforcing efficiency of the fiber in time makes its use in composite active for a short period of time only, such as handling reinforcement, shrinkage and cracking reinforcement.

Dimension stability is reflective of the materials durability and serviceability properties under external environmental factors and internal resistance of the constituent materials. Reduction in shrinkage of fiber mortar is most significant during the early age of hydration.

Reduction in shrinkage of fiber mortar is most significant during the early age of hydration. Average reduction of 15-20% was observed for fiber reinforcement of 1-2% volume fraction. Optimum fiber volume for shrinkage stability is about 1-2% for a practical length of 10mm or aspect ratio of 100.

Restrained shrinkage is recognized as one of the causes of large percentage of cracks in concrete structural elements even prior to loading. Hence, examination of the cracking incidence of natural fiber composite under restraints was carried-out. The following observations are drawn.

1. The appearance of the first crack is much delayed
2. Tensile strain capacity under restraints are 5-20% larger compared to the unreinforced matrix at period of 24 hours to 7 days
3. The composite can sustain relatively large strains for longer period of time, giving chance for the matrix to hardened sufficiently
4. Crack widths are much smaller and enabled the transfer of stresses to other least stressed area of the concrete material.

5. CONCLUSION

The program shows the effectiveness of using new technology approach to age-old material like the natural fibers. Applications of technologies such as centrifuged method enabled the development of new concrete products with special qualities inherent to its method of production, and thereby advancing both material science and construction applications.

Findings showed that natural fibers are significant reinforcing material, and knowledge of both its limitation and potential will enable materials engineer to use it for special purposes. Significant conclusions drawn are:

1. Inclusion of natural fibers improved the toughness, impact resistance, ductility, and energy absorbing capability of the brittle matrix like a gypsum mortar.
2. Natural fibers like sisal and coir have satisfactory reinforcing capability in a hydraulically pressed gypsum based panel, and is comparable to that of other low-modulus fiber such as polypropylene and vinylon.
3. The natural fibers are adequate reinforcement in pre-cast pipe and thin walled sections cast by centrifuged method. The precast fiber composite elements have high toughness, ductility, and impact resistance comparable to a 3 mm wire mesh (50 mm on centers). Thin walled pipes and square sections where wire mesh reinforcement poses placement problems, the natural fibers reinforcement could be an alternative.
4. The durability characteristics of the natural fiber composites are presented.
5. The potential of natural fibers at low fiber volume fraction as shrinkage reinforcement is most significant.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Production of Low-cost By-product Fillers

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This paper will present information on an industrial research project which aims to develop low cost ‘by-product’ fillers as a replacement for high cost ‘primary’ fillers. The source of the ‘by-product’ fillers will be fine waste residues from crushed rock aggregate quarries, which will be upgraded by particle size-reduction and by the application of suitable low cost beneficiation techniques. The products under investigation are industrial paints, membranes, low-grade paper, asphalt and lightweight concrete blocks. The paper will give details of the properties of two types of waste under investigation (siliceous and calcareous) as well as some details on the beneficiation studies.

1 BACKGROUND

Mineral fillers are used in a wide range of commodities such as paper, paint, plastics, membranes, ceramics, plasterboard, geo-textiles, rubber, pet food, chicken feed, electrical cables and several construction materials. These fillers are fine grained materials (<2mm) which are extracted specifically for that purpose ('primary fillers') eg kaolin and calcium carbonate. Primary sources are used because applications such as communications paper and household paints require a mineral which has a high brightness level and good rheological properties. This necessitates high quality deposits and sophistacted processing technology to produce a consistent product. Such fillers are marketed at a relatively high cost, as the total production costs i.e. extraction and processing have to be recovered by the operator. However many applications such as packaging paper, marine paint, certain plastics, membranes, ceramics, tyres, and electrical cables as well as some construction materials for example asphalt, porous concrete and lightweight concrete blocks, do not require fillers of such a high grade. Unfortunately, in most cases the only fillers commercially available for these applications are the high cost ‘primary’ fillers. The aim of the project is to develop 'by-product' mineral fillers for these markets.

Modern society creates a considerable demand for industrial rocks and minerals, particularly crushed rock aggregates. During the production process large volumes of mineral residue (10%-25% of total output) are generated, much of which is fine-grained (“mud slimes” and “quarry dust”). This potentially valuble resource is mostly unused and it is essential that optimum use is made of these residues to meet sustainability criteria and improve the profitability of quarry operations, whilst creating added value products. At present these fine grained residues are either stockpiled on site or transferred away from the quarry for disposal at waste sites. The problem is particularly acute for quarries in environmentally sensitive locations. Although some limited commercial use has been made of fine residues, for example the separation of feldspar from crushed granite fines, little attention has been given to the use of residues as mineral fillers.

2 TYPES OF WASTE

This study is looking predominantly at two types of waste, siliceous from Leahill Quarry, located at Adrigole in the South West of Ireland and calcareous from Mandra Quarry located west of Larisa in Northern Greece.

The deposit at Leahill was originally deposited as a sequence of delta sands with occasional bands of silt. This sequence was subsequently metamorphosed which had the effect of hardening the material. It is a grey/green/purple colour. In addition the beds are now vertically inclined resulting in more lateral variation than with depth. The quarry produces aggregates in the following size ranges 2-22mm - premium, 0-40mm - scalpings and 0-2mm dust. To make this later fraction acceptable to asphalt markets, the <75 micron is being removed using a fluidised bed.

Thin sections and XRD have shown the typical mineralogy to be >50% quartz, 10-15% chlorite and 20% feldspar. Chemical analysis is typically 70% silica, 14% alumina and 5% iron oxide.

The calcareous quarry at Mandra is located in an area of metamorphosed Triassic-Jurassic carbonates that belong to the Pelagonian zone. Both macroscopic and microscopic observations show the quarry has developed within calcitic marbles which in places (both laterally and vertically) are altered to dolomite and vary in colour (white to grey).

The grey rock types are mainly related to dolomite-rich calcitic marbles and constitute the lower members of the carbonate succession. Pure calcitic marbles (dolomite content 0-5%) usually develop lighter shades of grey up to off-white and white colours and constitute the upper members. Iron occurs in the deposit either as separate grains of geothite or as ilmenite staining, resulting in the residues having a pinkish hue.

3 THE PROJECT

The project includes two different quarry operators (representing the two major quarried rock types - siliceous and calcareous), three end users (industrial paint, packaging and toilet paper, asphalt and light weight concrete blocks), one equipment supplier (novel grinding equipment) and three research organisations.

Tarmac Fleming Quarries Limited is the siliceous quarry operator and also one of the end-users. The quarry is located in south-west Ireland, it has deep-water access and produces a siliceous aggregate with a high polish resistance suitable for premium grade sandstone. Between 20-2O5 % of the output is waste (<3mm). The <75 micron filler/dust is not currently saleable and is both an environmental and economical problem. A fluidised bed has been installed so there is some flexibility in classifying the material. The main benefit of the project to Tarmac Fleming will be to find a viable economic outlet for this material avoiding the need for landfill. The site has been geologically mapped to ensure a consistent quality of dust is maintained. Doriki Construction and Industrial Corporation is the limestone aggregate producer, located in Larisa, Northern Greece. The company have invested in a reconstruction of their crushing plant. Their main concern is the very fine (<1mm) material that has been removed so that high strength concrete can be produced. They are looking to find end users for the fines, manufacturers of paint and asphalt membranes being their main targets.

The British Geological Survey is the UK centre for earth science information expertise and research work. It is part of the Natural Environment Research Council. Its work relates directly to mineral, energy and groundwater resources, land use, geological hazards and protection of the environment. In the scientific research and development undertaken in support of this study, BGS will assist Tarmac Fleming in evaluating the quarry fines from Ireland in addition, they will look at other quarry fines (e.g. igneous rock and sandstone material) from quarries in the UK. They will also undertake beneficiation tests of the siliceous residue materials. The Greek Institute of Geology and Mineral Exploration (IGME) was established 44 years ago and is the official technical adviser in geo-scientific matters for Greece. The main role of IGME is the geological study of Greece and the exploration and evaluation of its mineral raw material and groundwater resources. The Department of Mineral Processing and Metallurgy will undertake beneficiation studies using both modern and traditional techniques and will research the criteria to exploit economic deposits. IGME and its predecessors have experience with different raw materials, and will benefit this study in the areas of mineral processing, ultra fine grinding of raw materials and support to the end users. IGME will predominantly undertake the research relating to the calcareous quarry operator.

Lodestone, an SME, is the supplier of novel grinding equipment and is licensed to operate the equipment known as a 'vortex grinder'. A company called Next Century Technologies is the patent holder for the vortex grinder, a trust set-up to protect its inventors. The vortex grinder has only one moving part, the rotor that creates vortices comminuting the material before it hits the impeller. This equipment has been installed at CRE (previously The Coal Research Establishment in the United Kingdom) where it will run large-scale tests. The speed and load will be varied to determine the optimum operating conditions.

Yannidis Brothers, established in 1932, mainly produces decorative, industrial, marine and car paints as well as asphalts, membranes (bitumen and roofing felts) asphalt emulsions and mastics. It has 20% of the market share in Greece with specialist paint and bitumen products and asphalt membranes. They are participating in the project to find a low-cost filler that benefits both the company and the environment. Their plant covers an area of 53,000 m^2 and the company has a turnover of ε (EURO) 50 million. Komotini Paper Mill S.A. (ELINA) was established in Greece in 1979. The company is involved in the production of tissue paper products (lavatory paper, kitchen towels, serviettes etc) and cardboard. The company employs 167 people and has a production capacity of 8000 tonnes per annum of tissue paper (5% of the Greek market) and 9600 tones per annum of kraft paper (4% of the

Greek market). Komotini is involved in several environmental initiatives which include recycling, pulping of annual non-wood plants such as kenaf and okra and biodegradation of plastics.

The first tasks to be undertaken were field studies and the collection of samples at both quarries, evaluation of the samples and then testwork will commence at both laboratory and pilot scale.

Existing production practices at both quarries (Tarmac Fleming's at Leahill in Ireland and Doriki's at Larisa in Greece) have been assessed. Samples have been taken to assess the variability in the quality of current residues and those that will be produced in future. Assessments have been made at laboratory scale to investigate the mineral and engineering properties of the residues to determine their quality and develop mineral processing techniques and flowsheets. Different techniques and flowsheets have been tested to up-grade the different quarry residues. Larger scale tests will investigate process options and generate scale-up data.

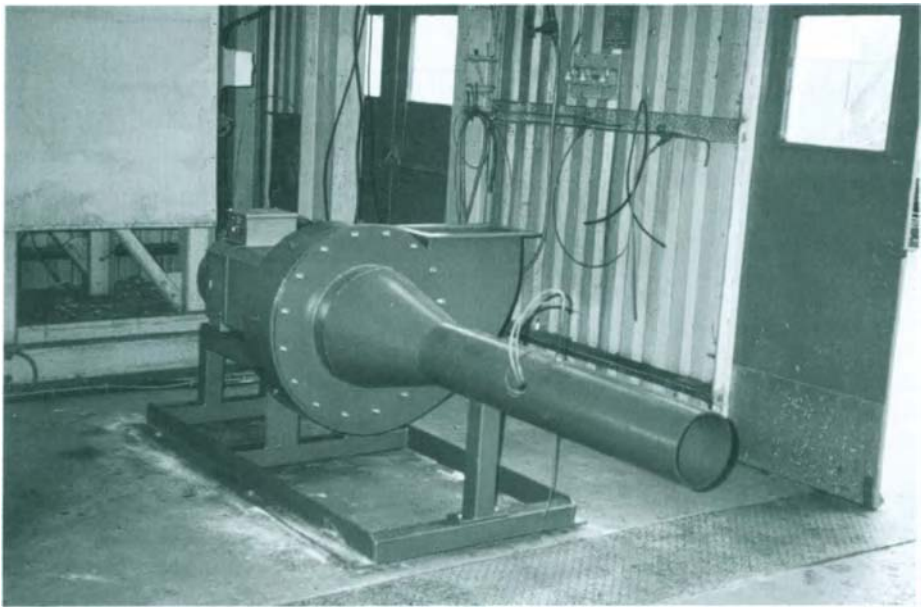

Figure 1 The Vortex Grinder installed at CRE

4 ACHIEVEMENT

Tarmac Fleming undertook the exploration drilling at Leahill Quarry where a system to record in detail which parts of the deposit were worked on an 'hour by hour' basis was introduced enabling exploration results to be correlated with production. The borehole samples permitted the quality of future residues to be assessed. A quarry plan with the borehole locations marked has been prepared and the geology of the deposit has been described.

Samples of residues and quarry raw materials were also taken from material produced before the installation of new plant at Leahill (which includes a fluidised bed to remove <75 micron material). These samples have been evaluated at BGS, for characterisation and testing.

Initial discussions have been held with both in-house (Tarmac) users and external users of fillers in concrete and asphalt to produce draft specifications.

Doriki in collaboration with IGME completed the sampling campaign with samples taken from current production (aggregates and fine material) and at the quarry near Larisa. Cores were extracted from both areas of current production and areas that will be quarried in the future. A field study of the quarry has also been completed and the borehole locations identified. A pneumatic conveyor system was selected as the most suitable to handle filler from the cyclone and bagfilter to processing units and manufacturers of materials sorting equipment have also been assessed.

Both BGS and IGME visited the quarries at Leahill and Larissa respectively to assist in the field studies and sampling. Whilst on site at Leahill BGS collected ten rock samples. These were grab samples taken from rock already broken at or close to the quarry face. In addition ten fines samples were collected from stockpiles and waste tips. During 1998, twenty further bulk samples of fines were collected from the newly commissioned processing plant and from dumps and stockpiles generated by the previous plant. An additional nineteen bulk samples of fines have been collected from ten quarries operated by Tarmac in Britain. These quarries work a range of siliceous and igneous rock types.

A literature survey undertaken by IGME provided information about the aggregate market in Greece, which indicated crushed rock constitutes the majority of aggregate production. The second main focus of the literature survey was the use of fillers in paints and plastics.

In collaboration with Doriki, IGME have completed the field study of the quarry describing its geology and that of the surrounding area. Some twenty samples were taken from the quarry, four from the quarry face and sixteen from a wider quarry area. Additional samples of fines from the plant were also collected.

4.1 Residue Evaluation

The rock and fines samples from Leahill Quarry have been logged and full characterisation will be completed. The petrography, mineralogy and chemistry has been reported for each rock sample. Results for the first ten fines samples have also been reported including the particle size analysis. The petrography of the rock samples was described using prepared thin sections of the samples. The mineralogy and chemistry were determined using X-ray diffraction (XRD) and X-ray fluorescence spectrometry (XRF) respectively. Particle size was determined using an X-ray sedigraph analyser.

Some typical results:

Leahill Rock 1/cjm494 Coarse Siltstone

Petrography

Greenish-grey in hand specimen, consisting of fine quartz grains (40-80 microns) in a fine matrix of chlorite, mica and quartz. Chlorite and mica mark out a faint lineation, the quartz grains are generally sub-angular to sub-rounded with a slight elongation parallel to lineation. Opaque mineral grains of Fe/Ti oxides occur disseminated throughout (<5%) up to 50 micron in size with an average size of 10-20 micron.

Mineralogy

Quartz	Na feldspar	K-feldspar
****	**	**
Mica	Chlorite	Calcite
**	***	*

**** = Dominant; *** = Major, ** = Minor, * = Trace.

Leahill Rock 4/cjm497 Fine sandstone

Petrography

Light-grey in hand specimen, consisting of closely interlocking quartz grains (average size 120-180 micron) with a small amount of interstitial fine-grained material. Quartz grains typically show a undulose extinction and triple-point/fused grain boundaries. A small proportion (<1%) of plagioclase feldspar, mica (<2%) and opaque mineral grains (<2%) also occur. Opaque mineral grains up to 150 microns, average size 30-100 micron.

Mineralogy

Quartz	Na feldspar	K-feldspar
****	***	**
Mica	Chlorite	Calcite
**	**	nd

**** = Dominant; *** = Major, ** = Minor, * = Trace, nd = not detected

IGME have reported the results of characterisation of the first twenty samples from Doriki's quarry. The petrographic features - colour, mineralogical composition, texture of the quarry rock samples has been determined. Size analysis and whiteness of the cyclone sample have also been reported. The following methods were used:

- optical microscopy
- XRD

The results of the characterisation of all twenty quarry samples have been reported and can be summarised as follows:

The quarry consists of medium crystalline to coarse crystalline calcitic marble with varying amounts of dolomite, it contains:

calcitic marbles (dolomite content 0-5%)
magnesium calcitic marbles (dolomite content 5-10%)
dolomitic calcitic marbles (dolomite content 10-50%)
calcitic dolomitic marbles (dolomite content 50-90%)

The marble colour varies from white to grey including intermediate shades, with the lighter colours predominant. The remaining minerals constitute accessory minerals and include muscovite, quartz as dispersed small grains, iron oxides as microscopic grains or staining and carbonaceous substances.

4.2 Beneficiation Studies Planned for Leahill Quarry Residues

The aim of the mineral processing is to improve the properties of a material to a state whereby it is suitable for an intended purpose. The quarry fines produced at Leahill quarry consists mainly of quartz and alkali feldspar, with approximately 15% chlorite and 5% accessory minerals (dominated by rutile). Removal of the chlorite and rutile would help to reduce the iron and titanium contents (4.7% and 0.9% respectively on average). Low cost fillers ideally have low iron and titanium, as these componenets are usually the cause of discolouration.

Mineral processing likely to be carried out by BGS on the Leahill Quarry residues includes:

Chlorite removal The chlorite occurs mainly as very fine grained particles, typically finer than 10 microns in diameter, with a small proportion consisting of discrete grains of chlorite up to 100 micron (most probaly altered mica). Size classiifcation is likely to be the most practical means of removing the fine-grained chlorite and trials will be conducted using both wet (hydrocyclones) and dry (air classification) methods. Other methods that will be considered include froth flotation, wet high intensity magnetic separation and chemical treatment.

Rutile removal The rutile occurs mainly as grains up to 100 micron in diameter. Gravity separation is probably the most practical means of removing the rutile (along with other heavy mineral present in the fines, such as zircon, monazite and leucoxene) and trials involving both wet (shaking tables) and dry (air tables) methods will be considered. Other methods that will be considered include froth flotation and electrostatic separation.

4.3 Beneficiation Studies Planned for Doriki Quarry Residues

The aim of the testwork is to devise new processing methodologies that will then be tested at larger scale. Following the characterisation of the samples an important factor will be the removal of iron from the material before grinding. The effectiveness of established mineral processing techniques using gravity and magnetic separation, air classification, particle size analysis and comminution will be tested.

5 MATERIAL EVALUATION

BGS will continue characterisation and beneficiation tests. It is necessary to determine the iron mineralogy using electron microscope and electron probe. Once the fluidised bed is operating satisfactorily at Leahill Quarry more samples will be taken and tested.

IGME will also continue laboratory scale tests and working in-conjunction with the end-users Yannidis Paint manufacture and Komotini Paper Mill.

5.1 Large Scale Tests

The objective of the larger scale tests is to investigate processing options selected at laboratory scale which will allow scale-up data to be obtained for use in techno-economic studies and subsequent commercial planning.

Lodestone will run trials using the 610mm vortex grinder which has been installed at CRE. Each trial will involve several runs to optimise the operating parameters. It contains a high speed rotor (5000rpm) and air trials with a 85kW motor have shown it pulls $200m^3/s$.. The next steps will include noise measurements and installation of acoustic housing. Also the comminution mechanism will be investigated and the feed system designed.

Previous trials using 38mm material have shown it reduces material to a d_{90} of 75 microns in one pass. Other large scale tests will be undertaken by both quarry operators. Using filler material produced by the two quarries the endusers will develop a test programme to evaluate the materials. Yannidis will use these materials in paint to define its suitability in the current production of paints and into its use in new paint products. Testing will evaluate the material as fillers extenders and as a leafing material for anti-corrosion purposes. Komotini Paper Mill will need to consider the following parameters when testing the material under normal plant conditions: type of filler, drainage of the pulper, paper moisture, machine speed, steam pressure and paper weight. If its possible two types of paper will be tested. Tarmac will test material in asphalt used in road making in membranes and in concrete blocks. Subsequent tasks will include evaluation of the products and re-evaluation of quarry practices and a techno economic assessment.

6 SUMMARY

The aim of the project is to investigate the use of quarry residues as low-cost fillers. Predominantly the work is centred on two quite different quarries geologically, although some ancillary work will be done on samples from other quarries. The quarries and research institutes have worked closely together undertaking field studies and sample characterisation. In collaboration with the end-users, the testing regimes have been devised to optimise their outcome.

The economics are highly favourable and it has been estimated that the production or around 400,000 tonnes per annum of by-product filler would generate ε 32 million/annum for the quarry operators and provide a saving of over ε 10 million/annumfor the user industries.

The partners of the project are participating in the EU network TRAWMAR (Targeted Research Action Waste Minimisation and Recycling), together a similar network EFCT (Environmental Friendly Construction Technology) plan to look at the quality assurance of concrete made using secondary materials.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Steel Fibers Made from Steel Cans in Concrete Engineering

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Recycling steel cans instead of making new products, uses so much less energy, pollution, water and water pollution. Only in Japan in 1994, about 472000 tons of steel cans could not been recycled. It means, such a huge amount of steel plates could be reused as steel fibers to reinforce plain concrete by considering many advantages of fibrous concrete. Reusing of *waste steel cans* as a construction material in plain concrete can improve concrete properties and also protect corrosion of reinforced concrete. In this matter, behavior of steel fibers made from steel cans in a transparent gel and concrete specimens were studied. Results of experiments showed that such fibers with average thickness of 0.25 mm increase flexural strength of plain concrete about 150 percent. Durability of these fibers under an accelerated and artificial aggressive environments showed that more than 75% of fibers in the concrete matrix were soundness. However, such fibers in contact with steel bars could cathodically protect corrosion of steel bars.

1. INTRODUCTION

Around our environments due to facilities of modern world steel solid wastes increase every year and this phenomena is an important problem which technologically needs to solve. Recycling/or reusing of wastes is one of option currently being utilized internationally to beneficially reuse waste. Many communities currently offer recycling programs to some degree. Several different types of materials can recycled. This could be either a curbside pick-up program or facilities where people can bring their material to a central location. As we know by now, many of the materials we use are recyclable. Some of the more common ones are newsprint, fine paper (computer papers, white paper), glass, plastic, aluminum and steel (tin) *cans*. Other than the advantage of recycling the amount of garbage that goes to the landfill, recycling has other benefits as well. The amount of energy that is required to recycle material is considerably less than to make a product from raw materials as well as reducing the pollution created in making a product. Also, using recyclable materials helps to reduce the depletion of our natural resources such as tree, aluminum and iron.

The recycling reduces energy waste, use of valuable raw materials, disposal costs, and pollution. Recycling steel cans instead of making new products, uses 75% less energy, creates

Table 1
Supply and demand of packaging steel in Japan

	Production *1000 tons*				
	1986	1987	1988	1989	1990
Tinplate*	1,552	1,724	1,768	1,750	1,627
TFS**	1,065	1,140	1,140	1,128	1,341
Total	2,617	2,864	2,908	2,878	2,968
	Demand *1000 tons*				
Domestic	1,564	1,710	1,748	1,892	1,948
Export	1,053	1,154	1,160	986	1,020

* TNS included
** Nickel plated steel included

86% less pollution, uses 40% less water and creates 76% less water pollution. In 1993, the domestic steel industry of America recycled 63.5 million tons of steel scrap. This steel scrap consists of everything from sardine cans and beat-up tricycles to abandoned jalopies and razed bridges. Since steel scrap is an integral part of the steel making process, reclaiming steel cans for recycling is important to steel industry [1].

Applying waste steel shavings as steel fibers in concrete technology to improve concrete behavior was already reported [2, 3]. Besides, deterioration of reinforced concrete associated with rebar corrosion has affected a great number of structures worldwide. The most common cases are parking garages, bridges and overpasses that demand extensive restoration and protection programs requiring multi-billion dollars annual budgets. In this study a new concept on recycling waste steel materials is presented. The new concept consists of applying steel fibers made from steel cans to reinforce plain concrete and/or to protect corrosion of embedded steel bars in the reinforced concrete members as a sacrificial anode.

2. TYPES OF STEEL CANS AND RECYCLING PROGRAMS

Packaging steels are broadly divided into tinplate and tinfree steel sheet (TFS). Table 1 shows the supply and demand of packaging steel in Japan [4]. For convenience tin nickel coated steel (TNS) is included under tinplate while nickel plated steel is listed under TFS.

Lightly Tin Coated Steel Sheet (LTS) is tinplate with the tin deposit reduced to about 0.3-0.8gr./m^2. During the baking process that follows lacquering, the iron-tin alloy layer grows, thus reducing the amount of pure tin. The tinplates produced in Japan have a minimum thickness of 0.245 mm and a coating weight of tin down to 2.8gr./m^2, which is 0.243 mm of

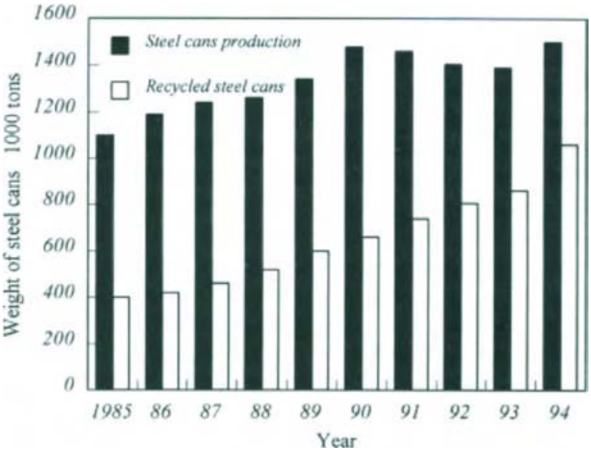

Figure 1. Production and recycled steel cans in Japan [6]

thickness and 1.1-2.8 gr./m^2 of coating weight for American tinplate.

The size of packaging business in Japan is roughly 1.4 percent of gross domestic product. In 1992, total shipment of packaging materials and containers in Japan amounted to US$53 billion in value and 22.085 million tons in weight which steel cans share was US$5.434 billion in value [5]. In 1994, 1.475 million tons steel cans was produced in Japan and only 1.03 million tons had been recycled which rate was 69.6%, however, till 2000 year, it is expected this rate increases up to 75%, Figure 1, [6]. It means only in 1994, about 472000 tons of used steel cans had not been recycled. However, this valuable materials could be reused without considerable cost as steel fibers. Using steel cans fiber not only can improve plain concrete characteristics but also can protect steel bars corrosion due to the role of sacrificial anode in the reinforced concrete and/or to minimize free chloride ions in the concrete matrix by forming quasi-stable ferrous.

3. EXPERIMENTAL PROGRAM

To find the capability of steel cans (SCAN) fibers in protecting of steel bars corrosion two phase of experiments have been done. The first phase was investigate to find the role of such fibers in contact with steel bars. This phase was done in ferroxyl transparent gel which allowed to observe the electrochemical reaction by naked eyes. The second phase was done in reinforced concrete specimens which exposed under an artificial severe conditions.

3.1. Ferroxyl Transparent Gel Environment

As stated above, in order to observe corrosion phenomena in steel cans (SCAN) fibers and steel bars, and the interaction between them, a modified ferroxyl reagent was used to accelerate corrosion process and simulate the concrete matrix. The ferroxyl reagent was a

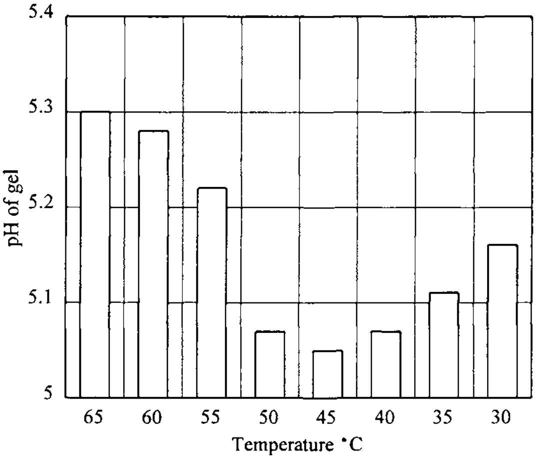

Figure 2. pH of ferroxyl transparent reagent gel

mixture of agar, phenolphthalein alcoholic-aqueous solution, potassium ferrocyanide solution ($K_3Fe(CN)_6$), 3% NaCl and 3% $CaCl_2$ dissolved in boiled distilled water with pH about 5.05-5.3, Figure 2. Applied steel fibers were prepared from steel cans (SCAN) and then fibers surfaces were already scratched about with natural sand for 5 minutes in order to allow electrochemical reaction in gel environment. The steel bars were deformed bars, 10 mm in diameter and 200 mm in length.

Two samples were conducted to study cathodic protection of SCAN fibers on steel bar corrosion. In the first sample 3 steel bars used without any fibers and for the second sample 3 steel bars were used with SCAN fibers which scattered around each steel bar.

The steel bars and SCAN fibers were degreased by acetone before setting in the ferroxyl gel. At the beginning of each test, 3-5 mm ferroxyl solution was poured into a petri dish and solidified, and then the first layer of the fibers or the steel bars were set on the solidified gel. The steel bars were set over the SCAN fibers and then more SCAN fibers were set over the steel bars. Most of the fibers were contacted with the steel bars. Finally 65°C ferroxyl reagent was poured over the bars to a level of 10-15 mm above the surface of them and left to form a gel. After the ferroxyl solution was cooled and gelled, observations were carried out of after 72 and 199 hours.

3.2. SCAN Fiber Reinforced Concrete Specimens

In order to observe exact behavior of cathodic protection of steel bars by SCAN fibers, fibrous reinforced concrete specimens were prepared. The experimental data were obtained using a lean mixture with 20 mm gravel, sand to aggregate ratio of 45%, normal portland cement. To accelerate electrolytic corrosion, 3 kg/m^3 NaCl by weight of concrete was added to concrete mixture during mixing. Slump of mixture was 7 cm and content of air was 8.5%. The SCAN fibers were space-oriented around steel bars within the matrix. All specimens were left inside the mold for 24 hours after casting, then stripped off the mold and were water cured

Table 2
Mix Design and Properties of Concrete specimens

Mixture Proportions						Mechanical and Physical Properties			
Sand kg/m^3	Gravel kg/m^3	Cement kg/m^3	Water kg/m^3	W/C	Air Entering lit./m^3	Ultimate Compressive Strength kgf/cm^2	Specific Gravity kg/m^3	Slump cm	Air Content %
850	1,070	280	154	0.55	0.22	198	2,210	7	8.5

at 21±1 °C for 27 days prior to testing or beginning of exposure. Mechanical properties of concrete were determined by Φ10x20 cm cylinders which yielded an average compressive strength of 198 kgf/cm^2 in 28 days, Table 2. Flexural strength of SCAN fiber reinforced concrete was determined by beam specimens of 50x150x350 mm in sizes.

Corrosion durability of fibers and their role to protect steel bars were carried out by reinforced concrete beams specimens of 10x10x40 cm in sizes. Two profiled steel bars of Φ 10 mm with 35 cm in length, were embedded at 2.5 cm cover thickness which connected to lead wires to measure electric potential of bars at necessary times. After 28 days of casting the specimens were put under wet-dry exposure conditions. The exposure conditions were selected in accordance with ASTM B-117 [7] with modifying to apply for reinforced concrete specimens. The wet portion used a flowing aerated recirculation 5% of sodium chloride aqueous solution which was showered over the surface of each specimens. The solution had an average temperature of 35 °C temperature and pH of 9.5-10.3 in the first week and then daily changing of saline solution was caused to decrease to pH 7.9-8.7 in later weeks. The wet-dry cycle consisted of 12 hours wet and 12 hours dry every operational day. Dry cycle consisted of 35 °C temperature of air circulation was flowing over specimens. Potentials of embedded steel bars were monitored periodically with respect to the Copper Sulfate Electrode (CSE) according to ASTM C 876-77 [8].

4. RESULTS

Results of this research include two sections. The first section presents results of corrosion protection behavior of SCAN fibers in the simulated ferroxyl transparent gel. The second section presents results of flexural strength of SCAN fiber reinforced concrete specimens and durability of SCAN fibers under aggressive exposure conditions and in contact with steel bars.

4.1. Corrosion and Cathodic Protection Processes in Ferroxyl Gel Environment

The main advantage which ferroxyl gel holds, is capability of colored monitoring of anode and cathode sites in an electrochemical process.

In production of steel cans an electrochemical treatment is used to improve paint adhesion and resistance to corrosion under coating films. Due to this matter, corrosion of SCAN fibers

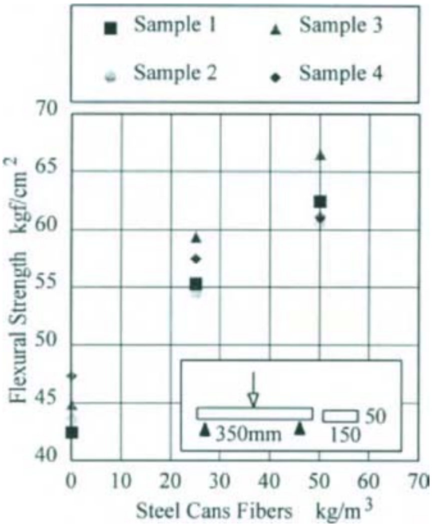

Figure 3. Flexural strength of SCAN fiber reinforced concrete specimens

in an aggressive environments is an important point. However, fibers with sacrificial anode role, need to have surface without any coating. According to this matter, without enough abrasion or scratch of coating materials, initiation of corrosion occurs delay. However, formation of anodic zones at the edges (cut parts) of fibers were completely active. On the other hands, sacrificial anode role of fibers starts from edges of fibers, and therefore SCAN fibers can protect corrosion phenomenon of the bars.

Formation of corrosion sites on the SCAN fibers surfaces which were not contacted with steel bars, were also observed. This behavior of SCAN fibers inside of gel matrix, showed that SCAN fibers can play the role of chloride ions removal by forming stable ferro-chloride products and decrease rate of free chloride ions even in concrete matrix.

4.2. SCAN Fiber Reinforced Concrete Specimens

Fibers made from steel cans which used in reinforcing beam specimens improved flexural strength of concrete respect to plain concrete, Figure 3. It means, such fibers which is possible to provide with very low cost, increased flexural strength of plain concrete to about 2 times. Thus, by this method besides of reusing waste materials to improve concrete strength for construction applications, the environmental protection is also provided.

The electrode potential of steel bars embedded in concrete mix was monitored at the first for 28 days after curing and then after 720 hours of exposure according to ASTM [7]. Figure 4 shows that the initial potential at 28 days after curing becomes more negative as the presence of added chloride and formation of passive layers, with values in the range -785 to -870 mV. With time, the potential tends to move in the positive, in spite of an ingress of moisture and

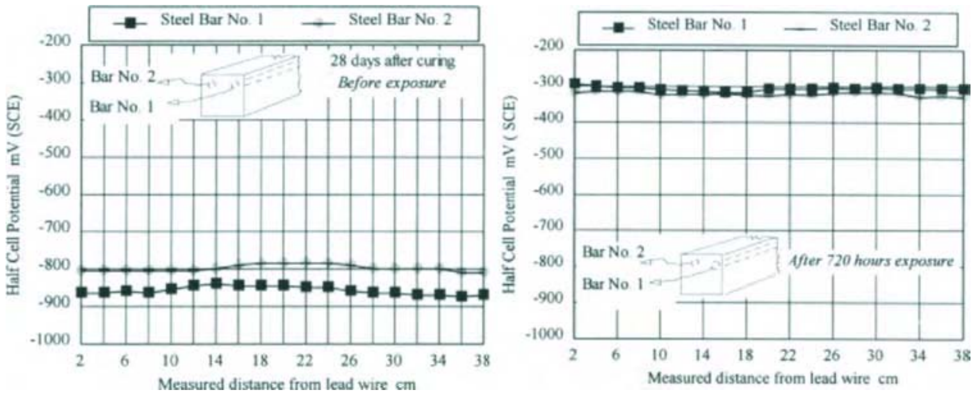

Figure 4. Corrosion potential of steel bars in concrete reinforced by fibers made from steel cans, before and after exposure

chloride. On the other hand, due to cathodic protection of SCAN fibers, there was not monitored significant negative potentials during exposure and after 720 hours respect to the more negative potentials of 28-day.

4.3. Visual Data

After the concrete specimens were broken open, the embedded rebar samples were examined visually for extent of coverage by corrosion products, nature of products, etc. After 720 hours under exposure conditions, the following results in the SCAN fiber reinforced concrete specimens were concluded.

1: Corrosion products as a rust with orange, brown and dark blue colors were observed on the surface and cut- sections of SCAN fibers.

2: At the depth of 22 mm from the exposed surface deterioration of SCAN fibers in contact with the steel bars were observed.

3: Debonding of coating layers of SCAN fibers and bonding of such layers to concrete surface were very interesting phenomenon. On the other hand, alkaline environment of concrete could not passivate fibers surfaces against corrosion.

4: Corrosion phenomenon in the steel bars was only observed in very small areas as spot zones with about 1.0x1.0 mm sizes in the steel bar No. 2. However, the steel bar No. 1 absolutely showed no-corrosion, Figure 5.

5: On the directly exposed surfaces of specimens, corrosion in more than 75% of fibers were observed.

6: About 20%-25% of SCAN fibers in the concrete matrix had been slightly/or fully corroded On the other hand, SCAN fibers showed durable behavior under severe conditions.

Based on the experiments results and visual observations, using steel fibers made from steel cans showed that according to fibers geometric, chemical properties and galvanic couple of

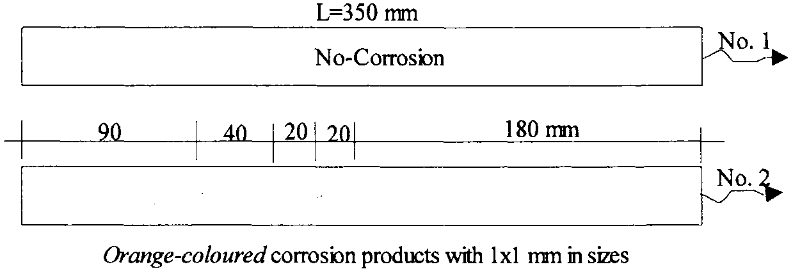

Figure 5. Corrosion of steel bars in concrete matrix reinforced with steel fibers made from cans

fibers in contact with steel bars, corrosion protection of steel bars were provided by sacrificial anode role of fibers.

Using steel fibers made from steel cans as a sacrificial anode to protect corrosion of reinforced concrete in a cathodic way have many advantages. These advantages are large surface areas, very low expansion volume of corrosion products, consume chloride ions due occurring corrosion inside the concrete matrix and the cheapest method for providing natural cathodic protection for the reinforced concrete members.

5. CONCLUSIONS

Reinforced concrete will undergo corrosion in some conditions. Anti-corrosion methods are available to help retardation or slightly to inhibit the corrosion of embedded steel. However, applying each methods depends on significance of structures, environment conditions, rate of chloride ions ingress and annual maintenance expanse vary in a wide area. Around our environments, there are many waste steels which can almost obtain without any charge such as steel cans. Reusing steel cans as steel fibers to reinforce concrete and to inhibit corrosion of steel bars showed the possibility of this idea. Observation of no-corrosion on the embedded steel bars in company with fibers made from steel cans was considerable. Besides, this kind of fibers improve plain concrete flexural strength and avoid crack propagation phenomenon and chloride ions ingress. To generalize this method and finding other important data, a long-term investigation is recommended.

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Waste Materials in Construction
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CARBONATION AND LEACHING OF PORTLAND CEMENT WITH VARIOUS BLENDING MATERIALS

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Degradation of Portland cement concrete, as well as the related protection and ensuring of Portland cement concrete structures against aggressive impacts by chemical agents, regardless whether this concerns liquid, gas or even solid phase under certain conditions, represents a complex problem of utmost importance for the economy in general, and especially for building construction and the construction industry. CaO leaching from Portland cement concrete in soft waters is one of the usual ways of Portland cement concrete degradation. Durability of steel in reinforced concrete is dependent mainly on the concrete protection layer. Usually, this layer has to be at least 4 cm. Also, pH value of this layer has to be higher than 7.5 to ensure alkaline media. But, CO_2 and moisture (acid rains recently) from the air makes this layer permeable to chlorine ions, such enabling steel corrosion. This effect is called concrete carbonation and is dependent of various factors, but mainly on the cement composition, w/c ratio and the concrete density. This paper presents results of CaO leaching content from Portland cements with various blending materials such as natural pozzolana and quartz river sand together with other characteristics of mentioned materials. Presented paper study also the changes produced by the carbonation when Portland cement, Portland fly ash cement and Portland blast furnace slag cement with various w/c ratios are exposed to the action of the atmosphere. The resistance to carbonation is significantly reduced when replacement of Portland cement by fly ash is higher than 15% and with higher w/c ratios.

1. INTRODUCTION

The carbonation of concrete is a matter of increasing concern since many structures have their surface directly exposed to the action of the atmosphere. Carbonation of concrete normally involves a chemical reaction between atmospheric CO_2 and that of cement hydration products if there is sufficient pore water. An important consequence is that the alkalinity of the pore fluid drops from a pH > 12.5 to a value of about 8. At this point the risk of corrosion increases significantly. The chemical changes induced by the carbonation create also variations of microstructure i.e. porosity. Carbonation can be defined as an ageing process where dissolved CO_2 in pore solution or free CO_2 in pores attacks the unhydrated or hydrated products of cement by a through-solution process or by a topochemical process, changing the chemical, mineralogical, microstructural and pore structural characteristics of the binding component of concrete. In cement based materials carbonation is able to change almost all components in paste comprising unhydrated, hydroxylated and hydrated phases [1-3].

Mechanism of cement and concrete corrosion is very complex, caused by equally complex physico-chemical processes, further supported in exploited objects by other factors such as raised temperature, alternate wetting and drying, freezing and thawing or mechanical influences. Water plays the main role in the process of concrete corrosion: solid and gaseous substances, even if potentially harmful to concrete, are ineffective unless dissolved in water. Therefore, water could be considered as the most important factor of the concrete destruction whose influence is manifold and varying, while its composition determines the type of corrosion. The extent of this influence would depend on the cement and concrete properties and various other factors influencing the course of the corrosion processes. One main class of concrete corrosion proceeds under influence of water whose initial hardness is low, as it is the case on dissolution of the cement stone components and its water leachout. Strengths of concrete are 50% lower at the 40% leachout of the limeish components, $Ca(OH)_2$ and CaO; at the 50% leachout, the concrete virtually disintegrates. This type of corrosion is known as a leaching corrosion [4,5].

In this paper, the leaching and carbonation were used to investigate the durability of concrete, mindful that concrete (cement) is the main matrix material for solidification/stabilization of various waste materials.

2. EXPERIMENTAL

Raw materials used for cement production for the carbonation and leaching tests were as follows: portland cement clinker 1 and 2, gypsum, blast furnace slag, tuff 1 and 2 (natural pozzolana), river sand and fly ash. All materials were dried, crushed and separately graded in laboratory mill with steel balls (capacity was 50 kg).

Raw materials were ground on following purpose specific areas:

1. Portland cement clinker 1 and 2	3000 - 3500 cm^2/g
2. Gypsum	3500 - 4000 cm^2/g
3. Slag	3000 - 3500 cm^2/g
4. Tuff 1	5500 - 6000 cm^2/g
5. Fly ash	5500 - 6000 cm^2/g
6. River sand	3000 - 3500 cm^2/g
7. Tuff 2	5500 - 6000 cm^2/g

Such provided materials were then homogenized in laboratory antistream agitator for powder materials and the following cements were prepared:

1. Portland cement PCK (97 % mass. portland cement clinker (PCC1), 3 % mass. gypsum)
2. Portland cement PCK1 (82 % mass. PCC1, 3 % mass. gypsum, 15 % mass. slag)

3. Portland cement PCK2 (82 % mass. PCC1, 3 % mass. gypsum, 15 % mass. tuff 1)
4. Portland cement PCK3 (82 % mass. PCC1, 3 % mass. gypsum, 15 % mass. fly ash)
5. Portland cement PCK4 (67 % mass. PCC1, 3 % mass. gypsum, 30 % mass. slag)
6. Portland cement PCK5 (67 % mass. PCC1, 3 % mass. gypsum, 30 % mass. tuff 1)
7. Portland cement PCK6 (67 % mass. PCC1, 3 % mass. gypsum, 30 % mass. fly ash)
8. Portland cement - 1 (97 % mass. portland cement clinker (PCC2), 3 % mass. gypsum)
9. Portland cement - 2 (67 % mass. PCC2, 3 % mass. gypsum, 30 % mass. river sand)
10. Portland cement - 3 (67 % mass. PCC2, 3 % mass. gypsum, 20 % mass. river sand and 10 % tuff 2)
11. Portland cement - 4 (67 % mass. PCC2, 3 % mass. gypsum, 15 % mass. river sand and 15 % tuff 2)
12. Portland cement - 5 (67 % mass. PCC2, 3 % mass. gypsum, 10 % mass. river sand and 20 % tuff 2)
13. Portland cement - 6 (67 % mass. PCC2, 3 % mass. gypsum, 30 % mass. tuff 2)

Chemical composition of tuff 1 and 2 and fly ash used for cement production was determined by JUS B.C1.018. Pozzolanic activity of tuff samples with lime was examined in accordance with the same standard. Chemical composition of granulated blast furnace slag and cements was determined by JUS B.C8.020. Chemical composition of the river sand was determined by usual analytical method (silicate analysis by an alkaline melting). Physico-chemical properties of cement were determined by JUS B.C8.023 and JUS.B.C8.024. Mechanical properties of cement samples - flexural and compressive strengths, were determined by JUS B.C8.022. with different w/c ratios. The cement mortar flow was determined according to the standard JUS B.C8.042 and linear deformations were determined according to the standard JUS B.C8.029.

2.1. Leaching test

Lime leaching from cement mortar surface was determined by immersion of sample with standard content (cement : sand = 1 : 3, w/c = 0.50), dimension of 40 x 40 x 80 mm, in 500 ml distilled water in glass tank of 600ml volume, which has a glass cover. The glass tank was not moved during the test. After each determination, 500ml fresh water was added. Before measuring, samples were cured for 7 days in a humid atmosphere ($t = 20 \pm 2°C$, $RH > 90\%$). CaO was determined in cumulative water mass (500 ml) by titration with $KMnO_4$. Several results were compiled and total cement in the samples estimated.

2.2. Method for the determination of the carbonation depth

Carbonation depth was measured at the sample 40x40x160 mm, with standard content and different water/cement ratios. Prisms were cured 7 days in the humid atmosphere ($t = 20 \pm 2°C$, $RH > 90\%$), and then stored (until 90 days) in the air ($t = 20 \pm 2°C$; $RH = 55 \pm 5\%$). Carbonation depth in concrete with CO_2 from the air was determined by pH indicator - phenolphtalein, at the freshly broken cross section area of the tested sample.

3. RESULTS AND DISCUSSION

Chemical composition of tuff 1 showed a high proportion of oxides $SiO_2 + Al_2O_3 + Fe_2O_3$ (84.97%) and low content of the other components, except CaO content - 17.1% and alkalies - Na_2O - 2.14% and K_2O - 3.08%. Tuff 1 was an active material with P5 class of pozzolanic activity. Chemical composition of granulated blast furnace slag showed a high content of SiO_2 and CaO, and MgO as admixture. Sulphide and MnO content were low [6-8].

Riversand is not an unusual mineral admixture in cement production. Chemical analysis of sand used showed that it was a high-grade sand (SiO_2 content - 82.03%) with low content of impurities. It was fine grained with a maximum grain size of 0.5 mm and minimum of 0.125mm. The sand sample did not contain undesired substances such as clay lumps, light particles or organic material. Mineralogical analysis of the sand sample, performed microscopically, showed that the most prevalent minerals were quartz (58.52%), and feldspar (31.57%). Ingredients are amphibole-pyroxene, biotite, chlorite and muscovite. Granite, zircon, magnetite, sandstone, coal and fragmented fauna residues were also present in minimal quantities.

Natural pozzolana - tuff is used occcasionally in the cement production. Chemical composition (Table 1.) showed high total oxides content $SiO_2 + Al_2O_3 + Fe_2O_3$, while the content of other ingredients were rather low except for CaO and alkalies. XRD results showed that the main mineral phase was zeolite clynoptilolyte followed by mica. Pozzolanic activity of the tuff 2 sample with lime was very good, categorized into P10 pozzolana class (Table 2.).

Table 1
Chemical composition of admixtures

Chemical composition, % mass	Admixtures				
	Tuff 1	Tuff 2	Slag	Sand	Fly ash
Moisture	2.11	4.02	0.28	0.11	1.47
LOI	6.68	8.55	1.11	3.37	5.68
SiO_2	63.67	65.02	36.35	82.03	50.85
Al_2O_3	16.38	12.74	12.03	3.59	21.65
Fe_2O_3	4.92	1.58	0.72	4.97	11.56
CaO	1.71	5.24	39.63	5.60	6.52
MgO	0.82	1.25	6.73	0.20	2.65
SO_3	0.00	0.09	1.58	0.00	0.05
S	0.00	0.00	0.35	0.00	0.02
Na_2O	2.14	1.96	0.87	0.15	0.30
K_2O	3.08	3.56	0.77	0.25	0.70
Insoluble residue	87.49	72.59	-	-	76.61
Hydrated water	-	-	-	-	34.56
CO_2	-	-	0.29	-	0.45
MnO	-	-	0.14	-	-

Table 2
Pozzolanic activity of tuff 2

Flexural strength	3.1 MPa
Compressive strength	13.4 MPa

Table 1 also presents the chemical composition of fly ash. SiO_2, Al_2O_3 and Fe_2O_3 content were high and CaO, MgO, alkalies and SO_3 content were low, so the fly ash was suitable for cement production. However, the loss on ignition (LOI) and hydrated water content were relatively high. Investigated fly ash sample is lignite fly ash. However, chemical composition of fly ash satisfy the conditions for quality of the Yugoslav standard JUS B.C1.018 and standard ASTM C 618 for class F, i.e., it is totally different from the usual composition of fly ash from lignite. SiO_2, Al_2O_3 i Fe_2O_3 content was high, while CaO content was very low for lignite fly ash.

The chemical composition of the cements is presented in Tables 3. and 4. All cements meet Yugoslav standard JUS B.C1.011. It is worth saying that the content of insoluble residue practically reflects the content of the amorphous phase which is the most reactive in reaction with $Ca(OH)_2$.

Table 3
Chemical compostion of cements

Chemical composition, % mass	Portland cement						
	PCK	PCK1	PCK2	PCK3	PCK4	PCK5	PCK6
SiO_2	21.42	23.25	18.63	18.23	25.97	14.35	16.30
Al_2O_3	4.36	5.38	4.01	4.33	5.94	4.49	5.05
Fe_2O_3	3.05	2.85	3.09	2.92	2.66	2.58	3.32
CaO	62.75	59.67	53.30	54.27	55.21	43.39	44.47
Insoluble residue	0.37	0.50	12.79	9.91	0.30	26.75	20.66
Moisture at 105°C	0.46	0.70	0.87	0.89	0.73	1.18	1.00
Loss on ignition	0.83	0.82	1.16	2.24	0.99	1.62	3.04
CO_2 in $CaCO_3$	0.68	0.41	0.89	1.01	0.56	0.95	0.82
Free CaO	1.07	0.32	0.32	0.11	0.32	0.37	0.11
CaO in $CaCO_3$	0.87	0.52	1.13	1.29	0.71	1.21	1.05
CaO in $CaSO_4$	1.09	1.14	1.09	1.02	1.15	1.11	1.02
SO_3 in $CaSO_4$	1.56	1.63	1.56	1.46	1.64	1.58	1.45
CaS	0.00	0.63	0.00	0.00	0.90	0.00	0.00
MgO	1.00	2.31	2.31	1.61	2.21	0.91	1.00
Alkalies as Na_2O	0.55	0.41	0.47	0.45	0.44	0.31	0.53
K_2O	0.42	0.26	0.29	0.30	0.25	0.20	0.35
MnO	0.05	0.05	0.04	0.04	0.04	0.04	0.02
FeO	0.10	0.17	0.20	0.42	0.24	0.17	0.49
P_2O_5	0.08	0.08	0.08	0.08	0.08	0.09	0.09
Cl^-	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 4
Chemical compostion of cements

Chemical composition, % mass	Portland cement					
	1	2	3	4	5	6
SiO_2	18.48	13.33	14.32	14.89	14.65	14.21
Al_2O_3	7.05	5.31	5.89	7.35	7.53	8.14
Fe_2O_3	2.57	1.70	1.56	1.83	2.08	2.02
CaO	58.80	58.53	40.29	40.51	43.10	43.44
Insoluble residue	1.73	27.47	25.04	22.90	21.65	19.51
Moisture at 105°C	0.61	0.60	1.00	1.63	2.02	2.67
Loss on ignition	0.89	1.40	2.18	1.93	2.01	2.46
CO_2 in $CaCO_3$	1.84	3.71	2.72	2.44	0.99	0.47
Free CaO	0.06	0.01	0.00	0.03	0.03	0.01
CaO in $CaCO_3$	2.35	4.82	3.47	3.11	1.26	0.60
CaO in $CaSO_4$	1.63	1.30	1.21	1.32	1.41	1.48
SO_3 in $CaSO_4$	2.33	1.91	1.73	1.89	2.01	2.11
CaS	0.00	0.00	0.00	0.00	0.00	0.00
MgO	2.21	1.80	1.81	1.81	1.41	2.41
Alkalies as Na_2O	0.69	0.50	0.64	0.77	0.77	0.92
K_2O	0.60	0.40	0.60	0.73	0.75	0.93
MnO	0.05	0.00	0.05	0.04	0.05	0.05
FeO	0.14	0.41	0.34	0.07	0.24	0.10
P_2O_5	0.07	0.08	0.07	0.07	0.09	0.08
Cl^-	0.00	-	-	-	-	-

Table 5
Physico-chemical properties of cements

Physico-chemical properties	Portland cement						
	PCK	PCK1	PCK2	PCK3	PCK4	PCK5	PCK6
Fineness							
- sieve residue at 0.2 mm sieve, %mass	0.60	0.50	0.30	0.10	0.30	0.60	0.10
- sieve residue at 0.09 mm sieve, %mass	2.20	2.30	2.50	2.10	2.00	2.60	1.50
Density, g/cm^3	3.13	2.94	2.90	3.02	2.84	2.77	2.89
Specific surface, cm^2/g	3397	3569	3285	4230	3489	3889	4680
Setting							
- standard consistence, %	24.2	24.5	25.8	26.8	25.0	27.8	29.6
- initial, h:min	05:30	04:45	05:00	04:45	05:45	03:30	04:30
- final, h:min	06:45	06:45	06:30	06:45	06:45	05:30	06:30
Soundness							
-Le Chatelier, mm	0.0	1.0	1.0	2.0	0.0	1.0	1.0

Table 6

Physico-chemical properties of cements

Physico-chemical properties	Portland cement 1	2	3	4	5	6
Fineness						
- sieve residue at 0.2 mm sieve, %mass	0.70	0.70	1.00	1.50	1.60	2.00
- sieve residue at 0.09 mm sieve, %mass	1.90	3.10	5.80	6.20	6.70	8.90
Density, g/cm^3	3.11	2.99	2.90	2.88	2.73	2.79
Specific surface, cm^2/g	3110	3560	3760	3880	3970	4010
Setting						
- standard consistence, %	26.7	27.0	26.5	27.5	28.0	29.8
- initial, h:min	2:45	3:00	2:30	2:00	1:45	1:30
- final, h:min	4:00	4:15	4:15	3:45	3:30	3:00
Soundness						
-Le Chatelier, mm	1.0	1.0	0.5	1.5	1.5	0.0
Flow, mm	174	160	148	135	129	117

Tables 5. and 6. presented figures characterizing fineness, density, standard consistency, setting time, soundness and flow of cements. The addition of tuff and fly ash raised the water demand for standard consistency, but had no significant influence on other characteristics. All characteristics were in compliance with Yugoslav standard JUS B.C1.011.

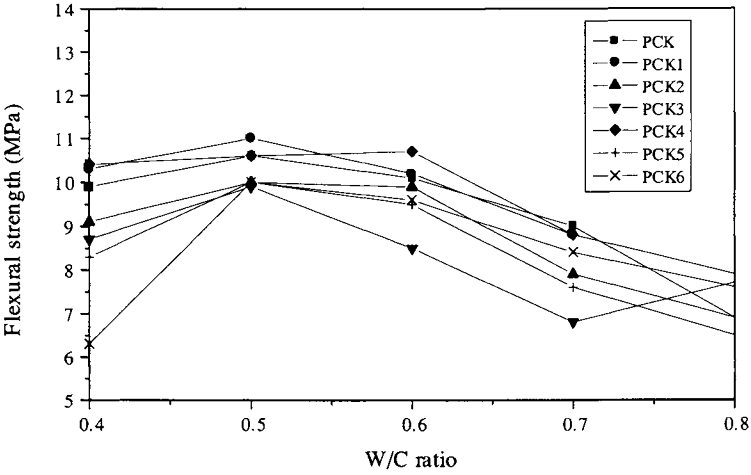

Figure 1. Flexural strength of cements after 90 days

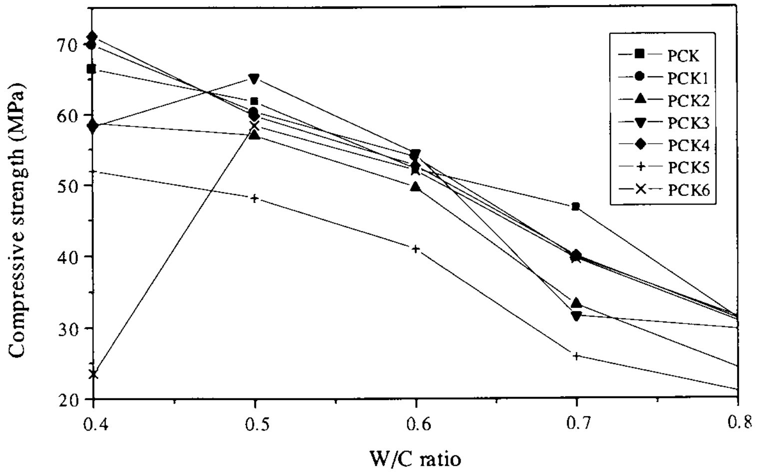

Figure 2. Compressive strength of cements after 90 days

Figure 1. and 2. gave values for flexural and compressive strengths of cements after 90 days with different w/c ratios. The best results were obtained for the 0.5 w/c ratio, because it is optimal for the quantity of water and for perfect moulding. With the decreasing of water content, the moulding became worse, and with increasing water content higher evaporation took place so the strength declined. Results were almost the same for all tested cements. Only cement with the higher tuff addition shown lower strengths for all applied w/c ratios.

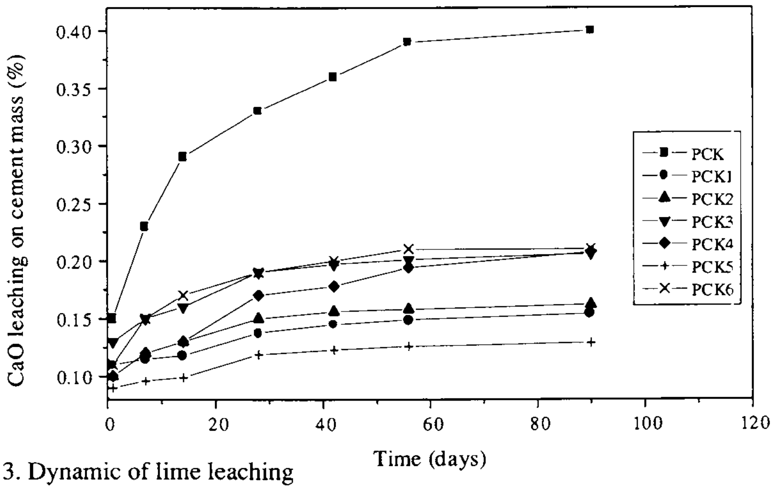

Figure 3. Dynamic of lime leaching

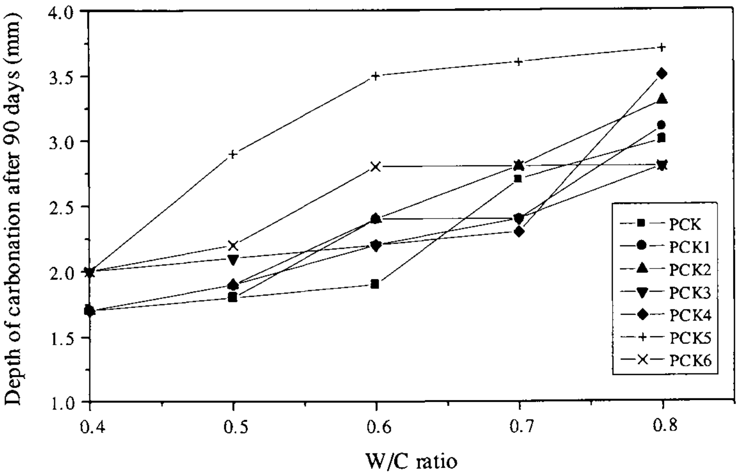

Figure 4. Depth of carbonation

Figure 3. showed that portland cement was the worst regarding CaO leaching. Consequently this kind of cement is not suitable for the soft underground and atmosferic waters which are very often present in our country. Leaching corrosion could be very strong in such cases. All other cements shown very good resistance to this kind of corrosion due to reactions between mineral admixtures (slag, tuff and fly ash) and clinker hydrated products.

The remainder of the experiment was now performed with the 0.50 w/c ratio.

Figure 4. showed that the carbonation is dependent not only on the kind of cement but on the w/c ratio also. The very best results were performed by the cement with the fly ash addition due to the protective layer formation on the sample surface. It is obvious that for this kind of cement w/c ratio was not significant regarding carbonation effect. The worst results were performed by the cement with the tuff addition so as by the portland cement.

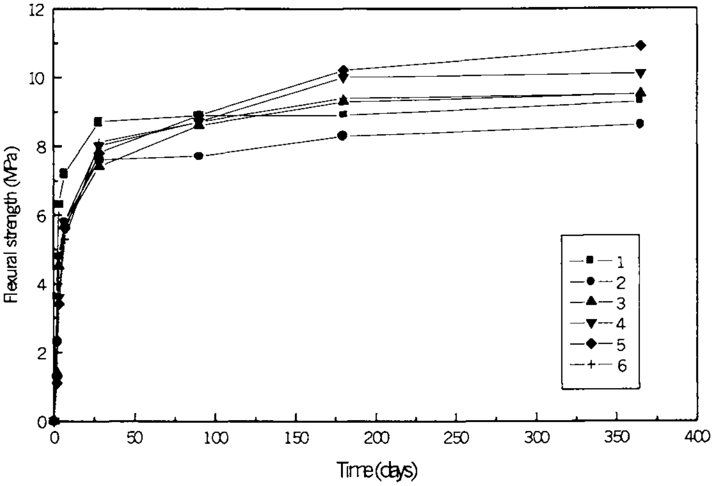

Figure 5. Flexural strength of cements after 90 days

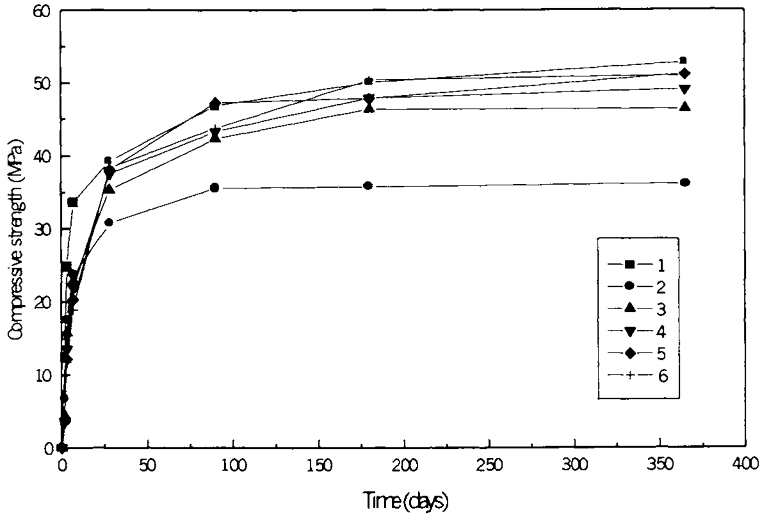

Figure 6. Compressive strength of cements after 90 days

As seen from the Figures 5. and 6., strengths of portland cements with and without mineral admixtures were very different. After 28 days the strength decrease was the highest in the cement with the addition of sand and the lowest in cement with the addition of tuff. In later ages, the results for cement with addition of sand were much worse, while addition of activated tuff practically maintained the strength equal to the reference case (cement without additives). Cement with the addition of 10% sand and 20% tuff, and cement with addition of 30% tuff were even stronger then the reference cement. This is the consequence of the sand's influence (improved workability and placeability) and pozzolanic effect of activated tuff.

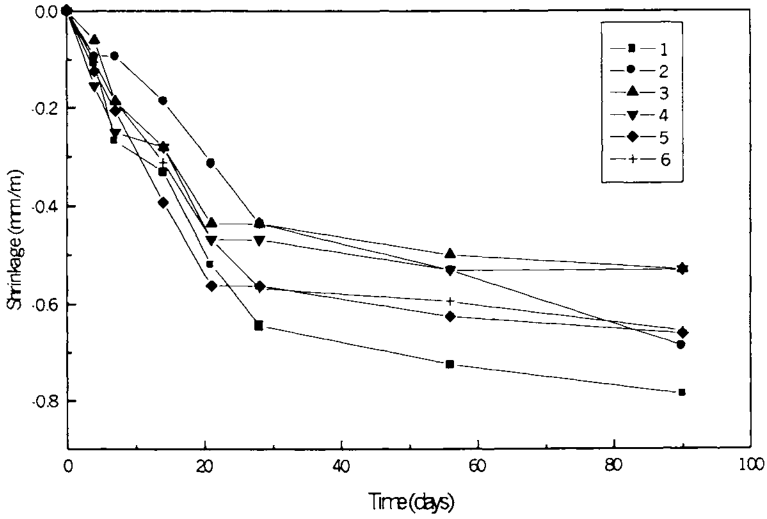

Figure 7. Linear deformations

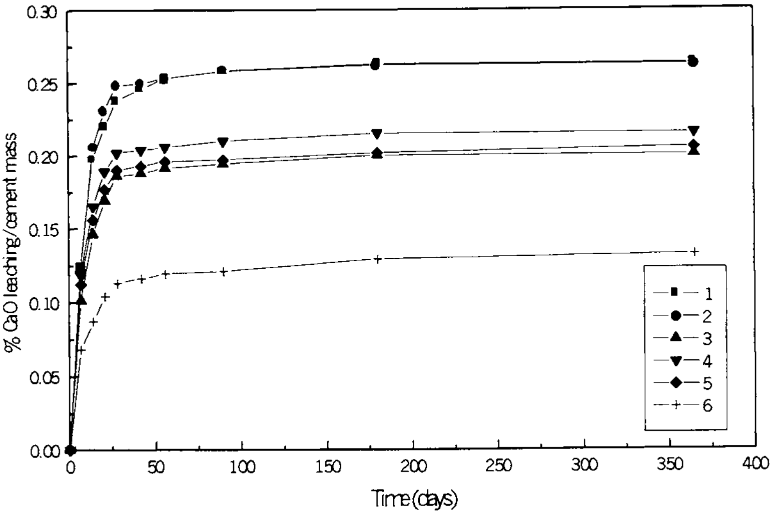

Figure 8. Dynamic of lime leaching

Sand and tuff addition produced positive effect on cement linear deformations - drying shrinkage (Figure 7.). This is primarily the consequence of influence of fine particles on improved particles arrangement in concrete. Besides, the amount of excess water leaving concrete prepared with cement containing sand and tuff, with the same w/c ratio, was lower comparing with the portland cement without admixture.

Lime leaching dynamics (Figure 8.) was only negligibly lower in admixtures with addition of sand comparing to the reference mix. However, tuff addition significantly decreased lime leaching from concrete. This phenomenon is particularly significant in concretes exposed to low hard waters where lime leaching could cause complete concrete degradation due to chemical corrosion. Obtained results were as expected because positive pozzolana influence is connected with its reaction with $Ca(OH)_2$ the main cement hydration product.

4. CONCLUSION

Based on presented results it could be concluded:

1. Mineral admixtures shown their best effects regarding CaO leaching and carbonation process. They also influenced other cement characteristics, especially strengths. It was obvious for all applied w/c ratios.
2. W/C ratio was significant for all tested cement characteristics, especially strengths and carbonation. But comparing cements with this kind of portland cement clinker with cements from other producers, this effect is much lower due to the C_3A content in this clinker. It is well known that this mineral has the significant influence on the cement behaviour regarding w/c ratio.

3. Lime leaching dynamics was only negligibly lower in cement with addition of sand comparing to the referent cement. However, tuff addition significantly decreased lime leaching from concrete. This phenomenon is particularly significant in concretes exposed to low hard waters where lime leaching could cause complete concrete degradation due to chemical corrosion. Results were as expected because positive pozzolana influence is connected with its reaction with $Ca(OH)_2$ the main cement hydration product.

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SOLIDIFICATION OF LEAD IONS IN PORTLAND CEMENT MATRIX

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Solidification/stabilization is world-wide accepted treatment for immobilization of wastes such as heavy metals and represents mixing of materials with binders and reagents in order to reduce the leaching of contaminants. The most commonly used medium in solidification/stabilization process is Portland cement, pozzolana such as fly ash from coal and solvent silicates. The purpose of this paper is to investigate the use of pure Portland cement and Portland cement with addition of 30% fly ash as binders for immobilization Pb^{2+} ions. Samples (1x1x6 cm) were prepared by mixing cement with water containing 10 000 mg/dm^3 Pb^{2+} and 30 000 mg/dm^3 Pb^{2+}. These samples were immersed in an aggressive acid solution (pH=4) and deionized water as reference. The temperature of acid solution and deionized water was 20°C and 50°C. Flexural strength of samples was measured. After 1, 3, 7, 14, 28, 35, 42, 49 and 56 days the concentration of toxic metal ions and Ca^{2+} ions in leachate solutions was determined by atomic absorption spectrometry. The end product of treatment, usually after sufficient curing, is solid monolithic material which, depending on characteristics of leaching, can be usefully applied or disposed of in a safe way.

1. INTRODUCTION

The process of solidification/stabilization is a widely accepted treatment/disposal process for a broad range of wastes, particularly those classified as toxic or hazardous which are not suited for normal methods of disposal and where special treatment is necessitated. Generally, for inorganic wastes, the hazard resides in the toxic and heavy metal content. Portland cement is a material found to be most useful for the purpose of solidification/stabilization due to its ability for fixation and immobilization of heavy metals [1].

For the immobilization of waste containing high concentrations of heavy metals, as in the case with the galvanization process, solidification is an acceptable treatment.

This is also consistent with the recent EU directions which refereed to the solid waste management. Solidification/stabilization processes will play more and more important role because in the near future only inert or stabilized waste should be landfilled [2].

Solidification/stabilization process means binding the hazardous material in the hydraulic binders for safe landfilling or their use in the civil engineering purposes. Various types of cement, pozzolana such as coal burning fly ash, lime, blast-furnace slag and similar materials are used as the stabilizing matrix mostly. Those stabilization techniques are used for the immobilization of inorganic or organic waste.

Stabilization procedure is relatively simple which represents one advantage of such way of waste management. If the waste is mixed with anhydrous cement and water, there is the possibility of ions incorporation in the cement structure during the hydrolysis process. Heavy metal ions could bind with the cement by the process of chemisorption, precipitation, surface adsorption, "capturing" inside the matrix, chemical incorporation or with the combination of these possibilities [3].

2. EXPERIMENTAL

Portland cement and Portland cement with 30% fly ash addition mixes were used. Chemical composition, physico-chemical and mechanical properties of cements were determined. The samples 1x1x6 cm were prepared by mixing cement with water containing 10 000 mg/dm^3 Pb^{2+} and 30 000 mg/dm^3 Pb^{2+}. The following mixes were prepared:

1. Cement paste 10: Portland cement (OPC) + distilled water
2. Cement paste 11: OPC + 10000 mg/dm^3 Pb^{2+}
3. Cement paste 13: OPC + 30000 mg/dm^3 Pb^{2+}
4. Cement paste 20: Portland fly ash cement (PPC) + distilled water
5. Cement paste 21: PPC + 10000 mg/dm^3 Pb^{2+}
6. Cement paste 23: PPC + 30000 mg/dm^3 Pb^{2+}

These samples were immersed in the aggressive acid solution (pH=4) and deionized water as reference. The temperatures of acid solution and deionized water were 20 °C and 50 °C. Flexural strength of samples was determined at the beginning and after 56 days in aggressive solution. After 1, 3, 7, 14, 28, 35, 42, 49 and 56 days the concentration of toxic metal ions and Ca^{2+} ions in leachate solutions was determined by atomic absorption spectrometry.

3. RESULTS AND DISCUSSION

Portland cement clinker potential phase composition is presented in Table 1. It can be seen that the C_3A content in the clinker is 9.46% which affects both the rate of hydration and sulphate resistance. Normal Portland cement is not resistant to the sulphate because of the relatively high C_3A content, which reacts with sulphate ions resulting in expansive compounds. Portland cement with the higher resistance to sulphates must have low C_3A content. Moderate to high content of mineral alite - C_3S (54.72%) is usual for the Novi Popovac Cement Plant and enables the addition of higher quantities of mineral admixtures without influencing the quality of final cement.

Table 1
Potential phase composition of Portland cement clinker

Potential phase composition, % mass	Portland cement clinker
C_3S	54.72
C_2S	18.47
C_3A	9.46
C_4AF	8.49

Table 2
Chemical composition of fly ash

Chemical composition,% mass	Fly ash
LOI	8.81
SiO_2	36.68
Al_2O_3	13.38
Fe_2O_3	4.78
CaO	29.44
MgO	2.82
SO_3	2.70
Na_2O	0.40
K_2O	0.97

Table 3
Pozzolanic activity of fly ash

	Flexural strength, MPa	Compressive strength, MPa
Pozzolanic activity of fly ash	1.3	6.9

Table 4
Chemical composition of Portland cement and Portland fly ash cement

Chemical composition,% mass	Cement	
	OPC	PPC
SiO_2	20.20	19.98
Al_2O_3	5.10	5.61
Fe_2O_3	2.39	2.39
CaO	62.80	55.23
Insoluble residue	0.65	6.85
Moisture at 105 °C	0.90	1.40
LOI	1.79	2.91
Free CaO	0.93	1.24
CaO in $CaSO_4$	3.48	1.67
SO_3 in $CaSO_4$	2.55	2.39
MgO	3.02	3.62
Alkalies as Na_2O	0.36	0.32
K_2O	0.74	0.70
Cl^-	0.00	0.00

Chemical composition of the mineral admixture - coal burning fly ash is presented in Table 2. Because of the low content of SiO_2 and high content of CaO this fly ash was not so suitable for the cement production. It also has the increased loss on ignition, yet complying with the Yugoslav standard JUS B.C1.018 [4]. It also could be seen that the MgO, alkalies and SO_3 content were in the limits of the mentioned Yugoslav standard.

Pozzolanic activity of the fly ash sample used (Table 3.), performed in the test with the hydrated lime according to the standard for P5 pozzolana class which means that it is acceptable convenient for cement production as the mineral admixture.

Both cements, Table 4., comply with the requirements of the Yugoslav standard JUS B.C1.011, concerning chemical composition. Portland fly ash cement PPC has the expected higher insoluble residue and the loss on ignition with respect Portland cement OPC because of the fly ash addition. Other constituents were not significantly changed by the fly ash addition.

Table 5
Physico-chemical properties of Portland and Portland fly ash cement

Physico-chemical properties	Cement	
	OPC	PPC
Sieve residue at 0.09 mm, %mass	1.4	1.6
Specific surface, cm^2/g	4000	4500
Setting		
-standard consistence, %mass	25.50	28.25
-initial time, min	55	125
-final time, min	145	205
Soundness		
-Le Chatelier test, mm	1.0	1.0

Table 6
Strengths of Portland cement and Portland fly ash cement

Strengths, MPa	Cement	
	OPC	PPC
Flexural strength:		
-3 days	6.9	5.9
-7 days	7.6	7.8
-28 days	9.2	8.3
Compressive strength:		
-3 days	36.6	25.5
-7 days	43.1	31.0
-28 days	52.0	40.7

Fly ash addition was obviously, Table 5., increasing the demand for the water for the standard consistence and prolonging the setting time, but had no influence on the other cement characteristics. All characteristics were in compliance with the Yugoslav standard JUS B.C1.011.

Values for cement flexural and compressive strengths after 3, 7 and 28 days are presented in Table 6. Portland fly ash cement PPC had lower strengths at all ages with respect to corresponding Portland cement OPC, a normal consequence of the fly ash addition. According to [5] the addition of fly ash is a slowing of Portland cement hydration in early ages, but later (at the age of 90 days and later) strengths of such cements are equalizing or become much higher than strengths of the corresponding Portland cement. In our case both cements complied with the requirements of the mentioned standard for the class 45. Flexural strengths of samples exposed to aggressive media were measured after 56 days. It could be concluded that heavy metal ions presence had no influence on strengths in such aggressive media [6,7].

Lead leaching concentration from the samples prepared with 10000 mg/dm^3 Pb^{2+}, Figures 1. and 2., was not above 0.1 ppm. Higher leaching was noted in the acid media, but also below 0.1 ppm, with worse samples of Portland cement than Portland fly ash cement. This was expected because it is known that the fly ash addition increase the resistance to acid media. It could be said that the lead in the concentration of 10000 mg/dm^3 was successfully stabilized in the Portland cement and Portland fly ash cement matrix.

Figures 3. and 4. show lead leaching results from the samples prepared with the 30000 mg/dm^3 of Pb^{2+}. It could be seen that the leaching was over 0.1 ppm, which is maximum allowed concentration for waterstreams [8], which means that the lead with this concentration couldn't be immobilized in such way that there is no danger of pollution, if such material is to be used in civil engineering (roads, embankments, foundations, etc.)

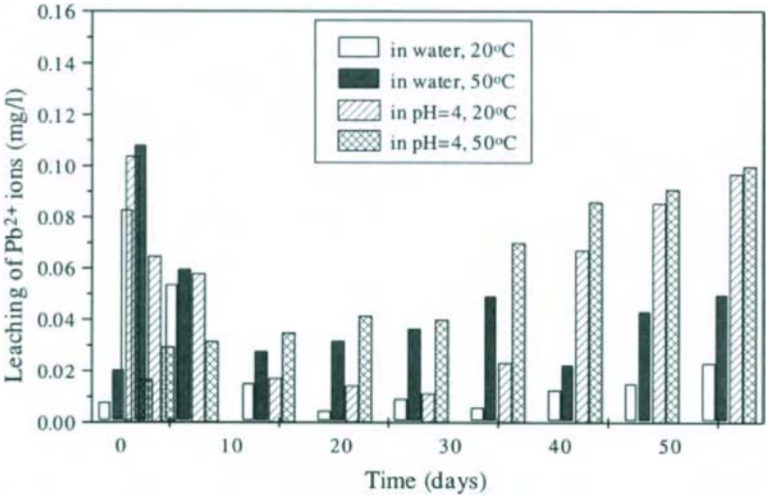

Figure 1. Leaching of Pb^{2+} ions from the Portland cement with 10 000 mg/dm^3 Pb(NO$_3$)$_2$, sample 11

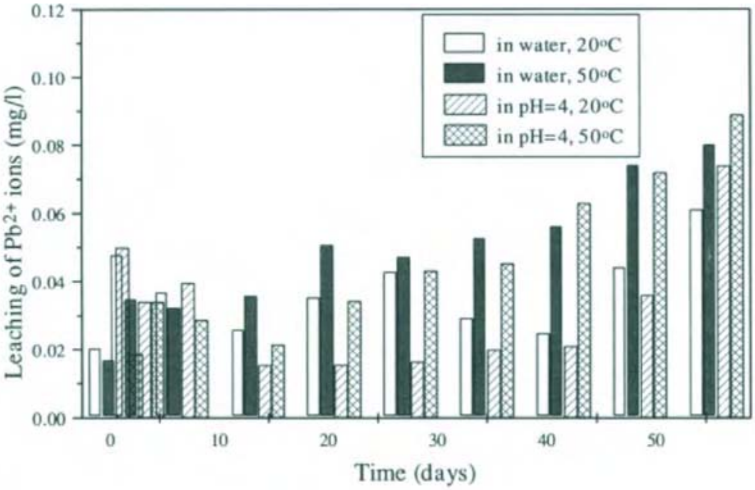

Figure 2. Leaching of Pb^{2+} ions from the Portland fly ash cement with 10 000 mg/dm^3 $Pb(NO_3)_2$, sample 21

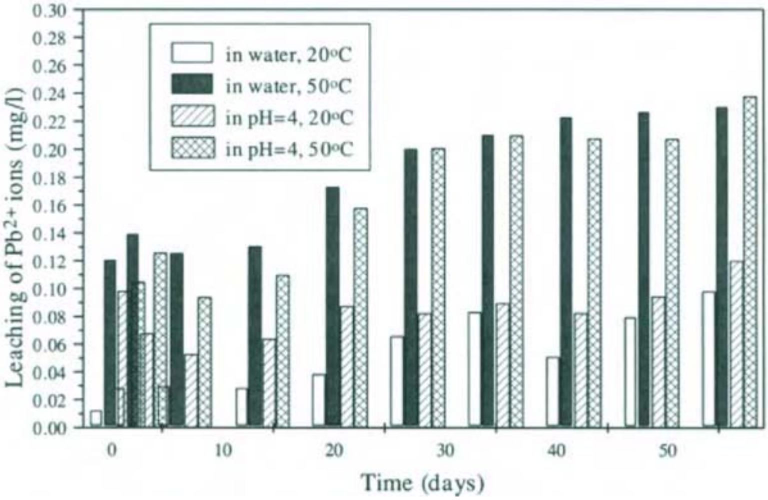

Figure 3. Leaching of Pb^{2+} ions from the Portland cement with 30 000 mg/dm^3 $Pb(NO_3)_2$, sample 13

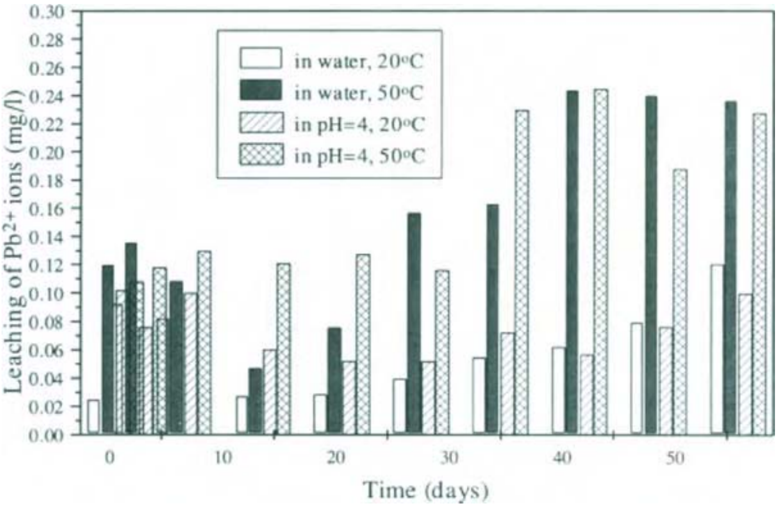

Figure 4. Leaching of Pb^{2+} ions from the Portland fly ash cement with 30 000 mg/dm^3 $Pb(NO_3)_2$, sample 23

Figures 5 and 6 shown diagrams of flexural strengths after 56 days in aggressive medium. In the begining, flexural strengths of samples which have heavy metal ions were lower than flexural strengths of control sample (sample 10). But, in later ages, this difference was lower. It can be concluded that presence of lead ions in cement matrix did not lead to decrease of flexural strengths in no one aggressive medium.

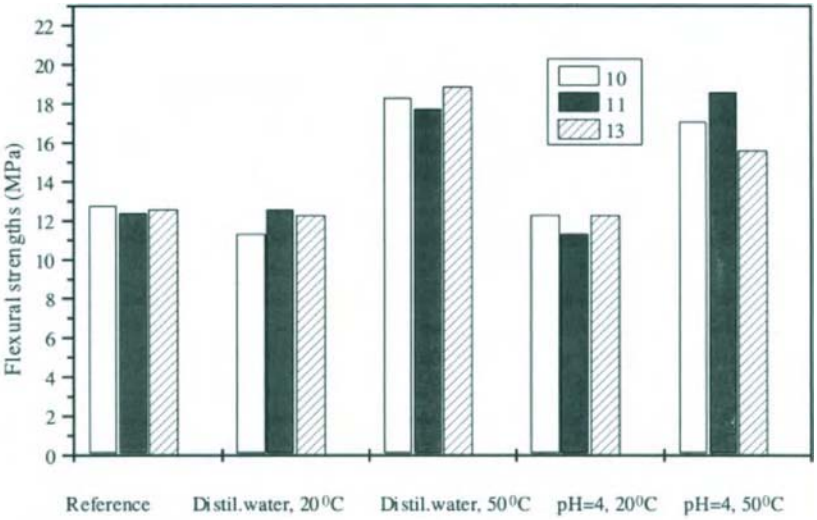

Figure 5. Flexural strengths of Portland cement after 56 days in various medium

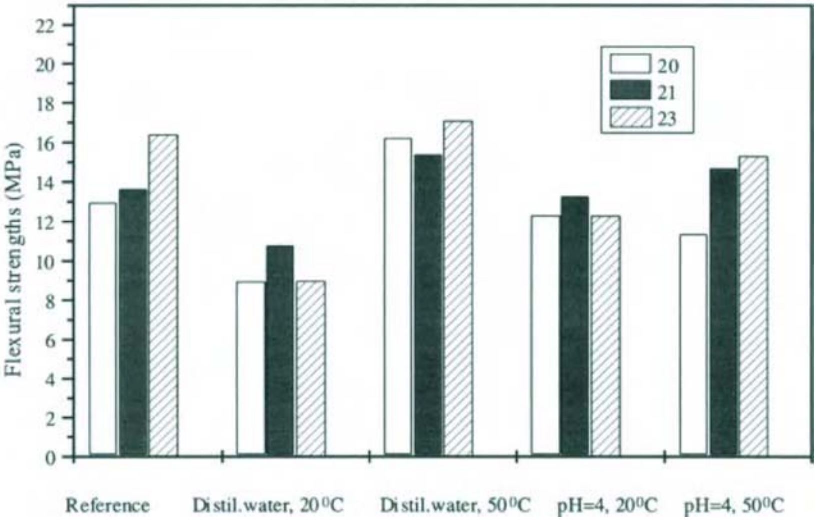

Figure 6. Flexural strengths of Portland fly ash cement after 56 days in various medium

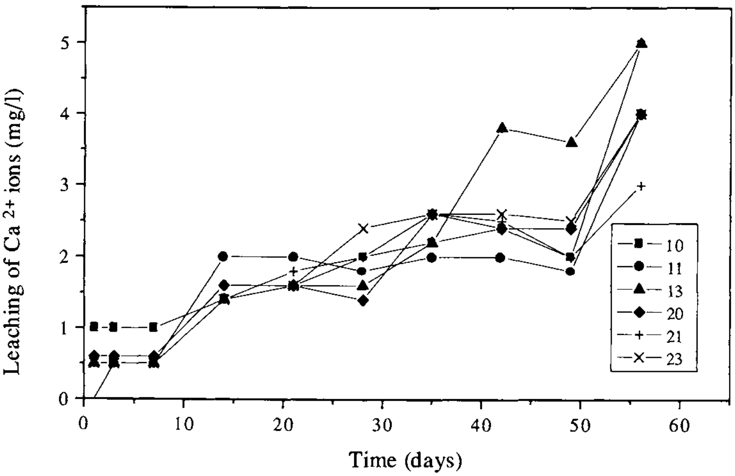

Figure 7. Leaching of Ca^{2+} ions in distilled water, T=20 °C

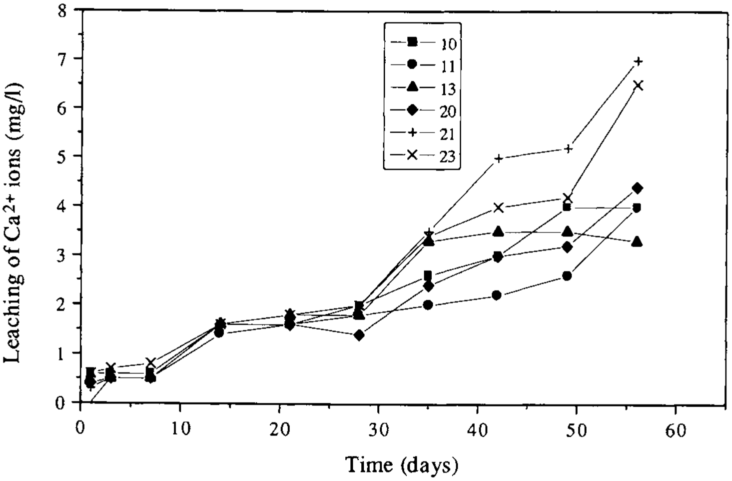

Figure 8. Leaching of Ca^{2+} ions in distilled water, T=50 °C

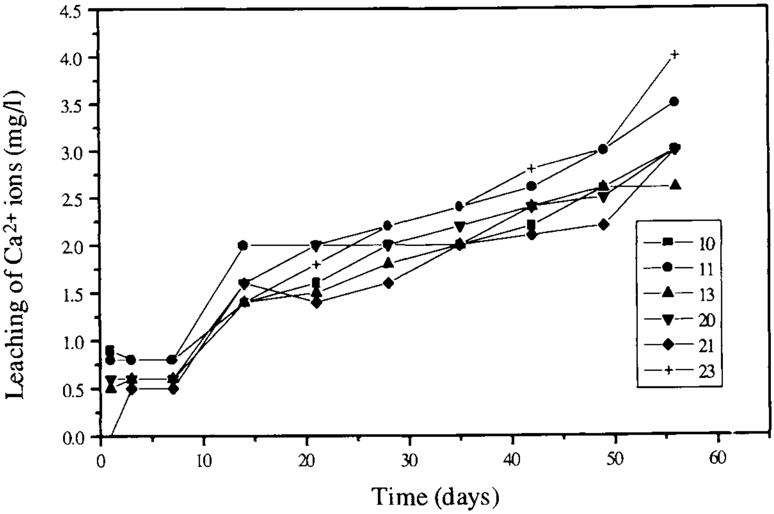

Figure 9. Leaching of Ca^{2+} ions in acid medium, pH=4, T=20 °C

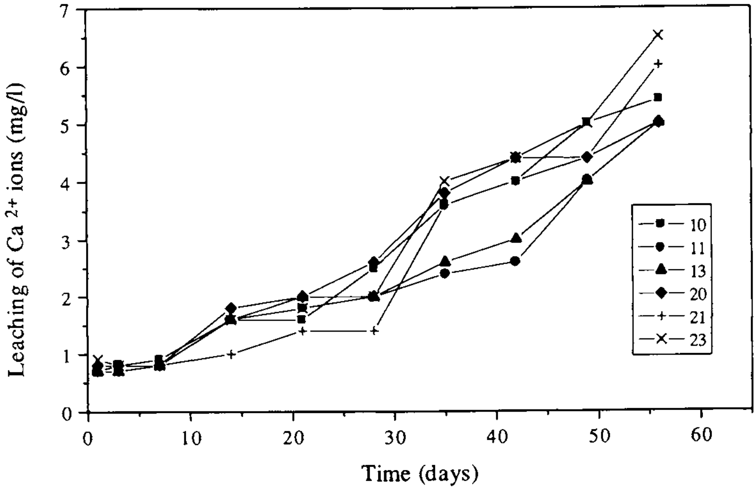

Figure 10. Leaching of Ca^{2+} ions in acid medium, pH=4, T=50 °C

Leaching of calcium from cement is, generally, increased when the samples were exposed in distilled water in relation to acid medium. Also, leaching of calcium is increased at a temperature of 50°C in relation on 20°C. Leaching of calcium is not dependent on lead ions immobilization (Figures 7-10.).

4. CONCLUSION

1. Successful stabilization/solidification of lead with the concentration 10000 mg/l of Pb^{2+}, in the cement matrix was achieved. Low concentrations during leaching showed that the heavy metal containing waste could be successfully stabilized and immobilized in this way and landfilled, or safely utilized as the building material.
2. Lead immobilization with the concentration 30000 mg/l of Pb^{2+} was not satisfactory regarding maximum allowed concentration of lead for waterstreams, which means that it couldn't be used in civil engineering (roads, embankments, foundations, etc.), but could be safely landfilled at the landfill for the hazardous waste.
3. Both Portland cement and Portland cement with the addition of 30% of fly ash achieved good immobilization, but Portland cement showed somewhat better strength results.
4. The presence of lead in the cement matrix with those concentrations didn't lead to decreasing of samples strengths. Lead showed good improvement in stabilization. Lead dissolution at low pH values corresponded closely with the loss of alumina, suggesting an ettringite or ferrite stabilization mechanism.

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Recycling and Up-grading Utility Arisings and Quarry Wastes for Highway Construction and Maintenance

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The principles of sustainable development require the minimisation of the production of waste, the efficient use of materials and the recycling of wastes. The UK government is committed to pursuing opportunities for the promotion of reuse and recycling of waste materials where they can substitute for primary minerals. The Minerals Planning Guidance Note (MPG6) published in 1994 proposed that an increasing contribution to aggregate needs should come from alternative sources, which include secondary materials, industrial by-products and wastes.

To address this theme, a consortium of Industrial partners, utility companies, private consultants, BRE , Manchester University and The DETR have combined their resources to develop novel technologies to enable cohesive, clay like materials to be recycled into useable aggregates for a range of applications.

The technology gained as a result of this research will enable the potential utilisation of millions of tonnes of utility trench arisings and quarry wastes generated each year. Key to the research is the use of industrial by-products as secondary slow cementing hydraulic binders, which will enable marginal materials and wastes to be treated and up-graded for uses where currently primary aggregates are used.

1. INTRODUCTION

Trenching and localised openings in roadworks and general urban infrastructure maintenance or new build can require the disposal of large quantities of excavated material and the import of similar amounts of primary aggregates. The unsuitability of these excavated materials is associated with their relatively high content of cohesive fine soils, clays and silts. The disposal cost of unwanted arisings to landfill is high and is expected to rise further. On the other hand, quarrying operations generate low grade products and wastes. The latter are known as overburden clays or scalping which are commonly used for quarry restoration. Consequently, both utility arisings and quarry wastes have a potentially significant value if they could be recycled and up-graded for higher specification end uses.

More significantly there are considerable environmental benefits to be gained by adopting recycling as the method of waste management as opposed to that of landfill disposal.

To address this theme Tarmac Quarry Products has formed a research consortium comprising; Scottish Power, Yorkshire Water, Ciba Chemicals, Tarmac Topblock, Babtie Group, Sitebatch Contracting, Building Research Establishment (BRE) and Manchester University. The overall objective is to use the combined skills and expertise of the consortia partners to develop novel technology to enable trench arisings and quarry wastes, in particular cohesive material (i.e. clays and silts), to be recycled into lightweight aggregates. The technology under development will enable the potential utilisation of millions of tonnes of quarry wastes and utility arisings generated each year. The adopted methodology specifically addresses the need for a cost effective treatment process by utilising wastes and by-products generated by other industries. This minimises the need to use relatively expensive chemical additives and also provides outlets for other industrial waste materials.

This paper summarises the progress made over the first year of a two year DETR funded research project .Specific details about clay materials are discussed and a brief description given of the adopted treatment philosophy. Some of the results gained during the extensive laboratory testing phase of the project are also presented.

2. CLAY SOILS STRUCTURE

Soils which contain a large proportion of very small mineral particles (diameter less than 0.002mm) are called 'clays'. Clays are characteristically plastic and smooth to the touch. In the wet state, clays are soft and cohesive. When dried out, clays shrink and crack and intact lumps become hard to break. Clays are generally characterised by the mineral type present in the clay particles. A ' mineral' can be defined as a 'naturally occurring chemical compound' and so includes a wide variety of solid geological materials which represent the simplest components of rocks [1].

There are two basic structure units which comprise the atomic lattice of clay minerals: the octahedral unit and the silica sheet. The octahedral unit consists of two layers of oxygen or hydroxyls in which aluminium, magnesium or iron atoms are embedded in octahedral co-ordination [2]. The silica sheet is made up of tetrahedrons, each consisting of one silicon atom held between four oxygen atoms [2]. The atoms in the octahedral and silica crystals are held tightly together by ionic and covalent bonds which are not usually broken under loading stresses.

Clay minerals have the ability to absorb certain anions and actions and retain them in an exchangeable state. Exchangeable cations are positively charged ions from salts in the pore water which are attracted to the surface of clay particles to balance the negative charge. The process is termed 'cation exchange' because one cation can be readily replaced by another of dual valence, or by two having half the valence of the original one. The ability of the clay minerals to absorb calcium ions is of fundamental importance in lime and cement stabilisation [3].

The water molecules that are held by the clay are called 'adsorbed water'. Three important factors affect the nature and extent of the adsorbed water [4] : (i) the charge carried by the clay,(ii) the valence of the exchangeable cation, and (iii) the concentration of electrolytes in the soil-water.

3. SOIL STABILISATION AND AGGREGATION

The concept of soil stabilisation varies enormously from the prosaic thoughts of a farmer who desires a process to stabilise the mud in his yard, to the abstract thoughts of the surface chemist or the discrete-particle physicist who may be concerned with the ideal properties of materials in the semi-solid state. From a soil mechanics point of view, the term 'soil stabilisation' means knowledge of the basic reasons for the physical behaviour of soil and the application of this knowledge to the control of physical behaviour. The stabilisation technique involves the alteration of the properties of a soil-water-air system to those desired for a particular application. This is achieved by introducing admixtures into the soil, ensuring that adequate drainage and compaction take place.

Soil aggregation is a form of soil stabilisation where admixtures are added to the soil but no physical drainage or mechanical compaction can be undertaken. The strength of the resulting synthetic aggregates depends on the effectiveness of the chemical reactions causing the soil particles to bond, dehydration and the reduction of air voids. Selecting the appropriate admixture combination and method of mixing are key influencing factors affecting the strength of the resulting aggregates.

The philosophy adopted at the outset and maintained throughout this research project is to utilise by-products and wastes generated by other industries to treat construction wastes, in particular clay soils. This has been achieved by means of a novel clay aggregation process, resulting in the production of lightweight aggregates. It is believed that the treatment process, which utilises existing mobile mixing and crushing plant, is innovative with limited research previously undertaken in this area.

4. STABILISATION METHODOLOGY

The addition of any stabilising agent usually affects the plasticity, compressibility and permeability of clay soils. The main interest in this project however is the improvement in soil strength and resistance to water. Increasing the strength is related to improvements in the effectiveness of particle bonding. Improvements in the water resistance of treated clay can be related to hydrophobic compounds created during the complex reactions between the various wastes and by-products used to improve particle bonding. A speciality chemical dispersed throughout the treated clay matrix, in low concentration, facilitates the final hydrophobic state .

The stabilisation process developed as a result of this research *(pending patent protection)*, involves the use of five additives. Additive 1 is a speciality chemical which is mixed into the clay to improve workability thereby facilitating the addition and reaction between three hardeners ie additives 2, 3 and 4. The process also involves the addition of a liquid polymer (additive 5) to further improve the treated clay's water resistance .

The experimental work revealed that the method of mixing is important to the strength of the end product. By introducing a predetermined amount of water to the clay material, a thick slurry could be produced. This is followed by the addition of a fixed concentration of additive 1 into the continuous mix to de-flocculate the clay minerals.

A pre-blend of additives 2, 3 and 4 is then added and thoroughly mixed, initiating two different types of chemical reaction; (i) primary bonding of the clay minerals occurs, as a result of a short term chemical reaction triggered by additive 2 which also forms a matrix encapsulating the dispersed fine particles of additives 3 and 4; and (ii) a secondary, slower, chemical reaction is initiated by the action of additives 3 and 4 resulting in the long term strengthening of the whole matrix over a period of several weeks and months.

The treated clay is left to cure at ambient temperature in protected stock piles for 28, 56 or 90days prior to crushing and screening into single size aggregates. The cure time depends on the final strength requirements. Dust generated as a result of the crushing process is recycled back into the virgin clay material about to undergo treatment.

5. EXPERIMENTAL WORK

Five different types of clays were considered in the experimental work : London Clay, Boulder Clay, Fire Clay, Marl and Shale. Each material was sampled from the same source at the same time. Preliminary tests consisting of x-ray diffraction, moisture content, atterberg limits and grading were carried out on each material. Also some compressive strength tests were undertaken on cubes made with untreated clay material.

Initially each clay was fluidised in a concrete mixer by addition of water followed by additive1 . Various concentrations of additives 2, 3 and 4 were subsequently added to each blend. Cubes were then made from each mix and left exposed to cure at 20c in the laboratory. These cubes were then tested for compressive strength at various ages. After testing, the cubes were crushed further to produce lightweight clay aggregates. These aggregates were then used in a typical concrete mix with sand and cement to form cubes for crushing at various ages.

6. RESULTS

This paper presents some of the results obtained on the compressive strength tests which were carried out on the cubes made from the various types of treated clay mixtures. The effect of the percentage of the combined additives (i.e. additives 2, 3 and 4) and the curing time on the compressive strength are shown in figures 1-4.

The results show a compressive strength gain in the range; 1.9 to 2.7 Nmm^{-2} at 28 days for all the clays treated with 10% combined additives. At 56 days the increase in strength ranges from; 2.4 to 4.1 Nmm^{-2} for all clays treated with 10% combined additives and at 72 days the range is 2.5 to 4.4 Nmm^{-2}. The inference from these results is that the main gain in compressive strength occurs around 56 days.

Interestingly, results for the Shale material show that there is an optimum level of addition for the combined additives beyond which the compressive strength decreases (Figures 1 and 2).

An independent mineralogical study was undertaken by Manchester University to assess the effect of the treatment methodology on the clay minerals. X-Ray Diffraction (XRD) and Thermogravimetric - Differential Scanning Calorimetry (TG-DSC) techniques were used to create a baseline for the raw/untreated clay materials. XRD analysis was used to study the compositional differences between the processed clay aggregates and their corresponding raw materials. Also, Scanning Electron Microscopy (SEM) was used to study the mineralogical

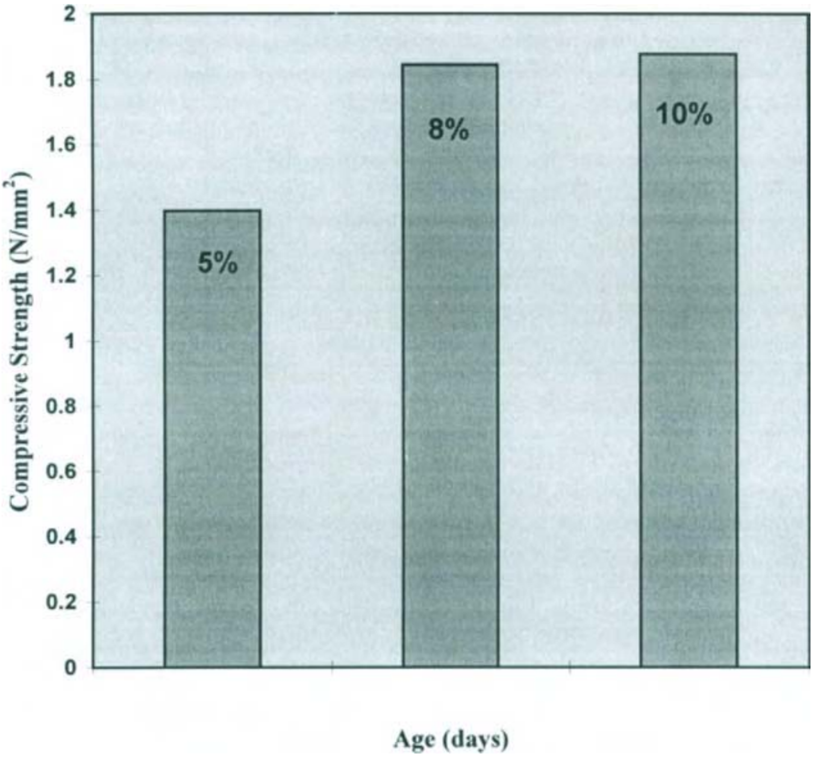

Figure 1 : Averaged Results on Marl Clay Treated With Varying Amounts of Additives and Tested at 28 Days

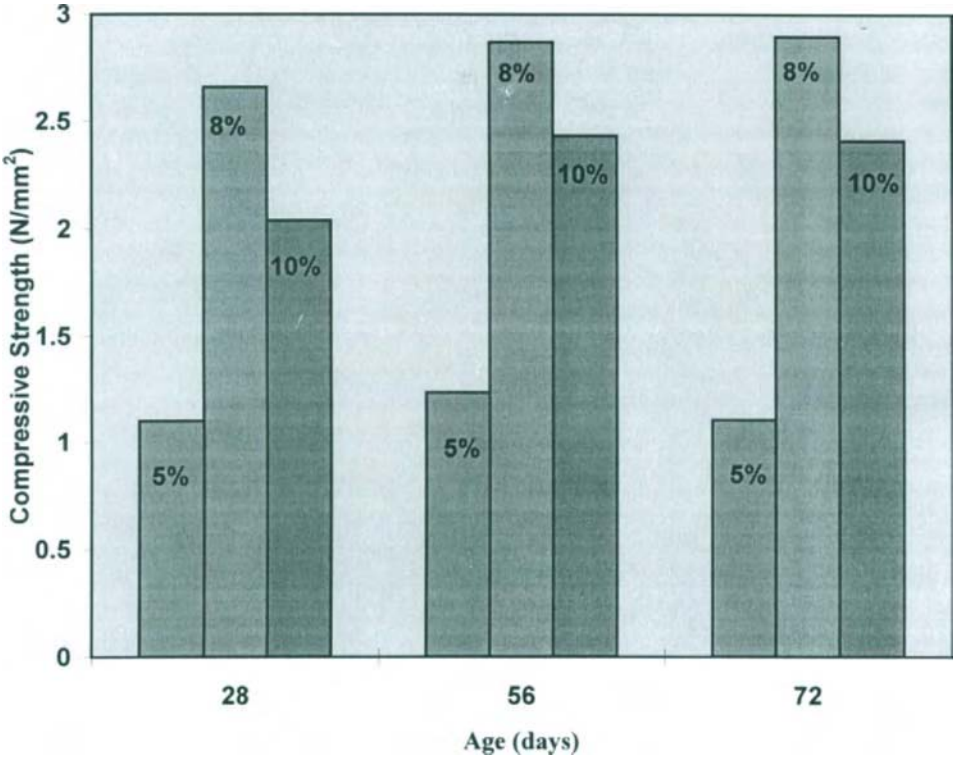

Figure 2: Test Results on Shale Treated With Varying Percentages of the Combined Additives

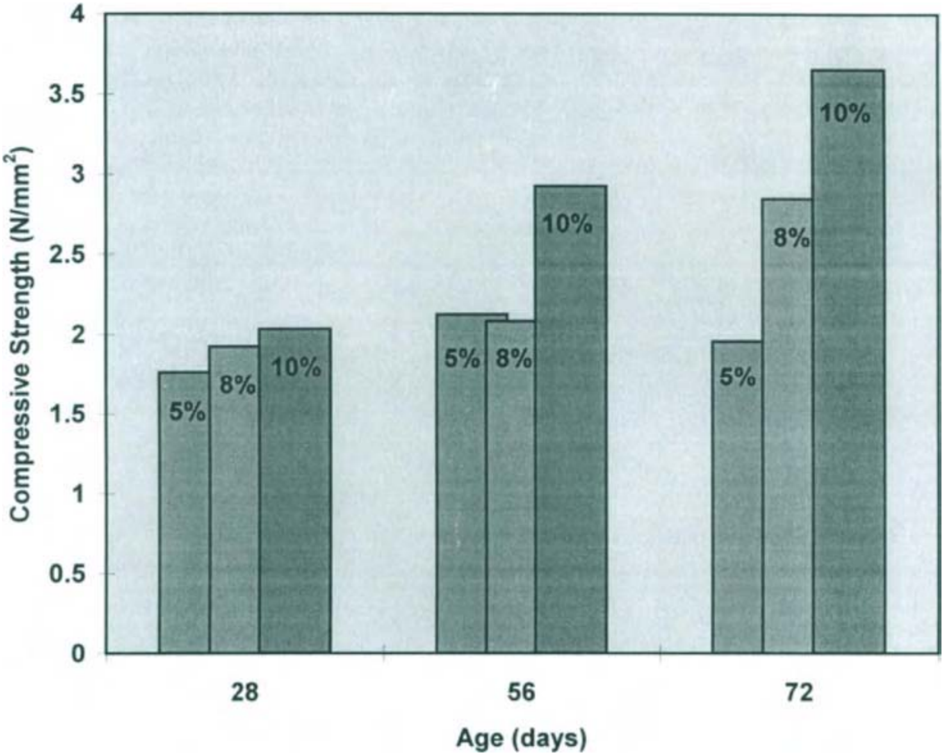

Figure 3: Test Results on Fire Clay Treated With Varying Percentages of the Combined Additives

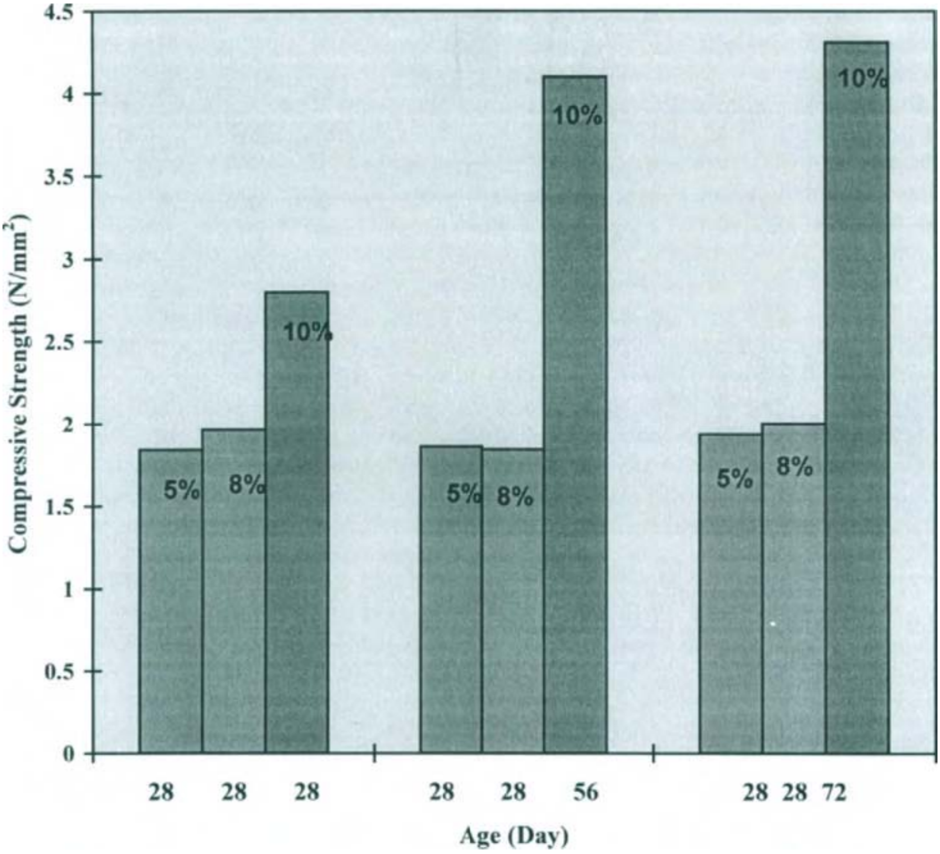

Figure 4: Test Results on Boulder Clay Treated with Varying Percentages of the Combined Additives

and textural differences between the processed clay aggregates and their corresponding raw materials. At this stage, to protect the confidentiality of the research, the results of this study cannot be published.

6. CONCLUSION

During the first twelve months of this DETR funded, collaborative research project, a novel process for the conversion of clay into lightweight aggregates has been developed. Results generated in the laboratory are sufficiently encouraging for the project to move onto the next stage ie pilot production trials, to assess the practical difficulties in converting theory and laboratory scale trials into practical reality. It is envisaged that this will be achievable whilst remaining within the overall project objective of developing an economic process capable of producing aggregates at competitive cost.

7. ACKNOWLEDGMENTS

The financial assistance from the DETR and the support of all the participating organisations is gratefully acknowledged.

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Progress Towards Achieving Ecologically Sustainable Concrete and Road Pavements in Australia

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Abstract: Historically, the concrete and road pavement industries in Australia rely heavily on the use of prime quality natural aggregates. Abundance of high quality natural fine and coarse aggregates, located close to major cities, prescription specifications and seemingly unlimited waste disposal sites, have contributed to this practice.

Despite the successful introduction of the industrial by-products of Fly Ash and Blast Furnace Slag products to concrete and road construction in the 1960's, it is only relatively recently that both government and private sectors have accepted the view that better utilisation of resources must be achieved. A more ecologically sustainable and responsible attitude is being adopted with respect to waste minimisation, utilisation of by-products, re-use of construction and demolition waste and improved energy efficiency.

Some of the issues and steps to be implemented in this regard are outlined, covering topics such as: recycled concrete aggregate, (RCA), concrete washouts, reclaimed asphalt pavement (RAP), manufactured sands, tunnelling materials, bottom ash and other similar products.

The research carried out, both in laboratory and in the field, demonstrates the suitability of such products in concrete and road pavement applications. It is concluded that some provisions in the current specifications and new performance based specification are necessary in order to accommodate more construction and demolition materials.

Key words: Construction and demolition, waste, recycled concrete, reclaimed asphalt pavement, bottom ash, manufactured sands.

1. INTRODUCTION

Every year, in New South Wales only, about 50 million tonnes of construction materials such as river gravel, crushed igneous or metamorphic rock, sand and structural clay is being used for construction. The total value of the materials extracted exceeds $500 million EPA (1).

For example, to construct one kilometre of a four-lane motorway with concrete pavement it requires 1,620 tonnes of cement, 7,800 tonnes of coarse aggregate, 3,240 tonnes of sand.

A similar road with an asphalt pavement requires 8,400 tonnes of roadbase, 3,600 tonnes of coarse aggregate, 2,400 tonnes of fine aggregate, 540 tonnes of sand and 300 tonnes of bitumen.

At the same time, there is a continued increase in the construction and demolition waste, the issue of waste management becoming more significant not only for the government, but for the construction industry as well.

In 1997, EPA (1) co-ordinated a census of construction and demolition waste disposed in parts of New South Wales with some indicative figures suggesting that the total tonnage of construction and demolition generated annually is approximately 1.5 million tonnes.

About 60% by weight of this waste is demolition work. There is not sufficient data on the amount of construction and demolition waste that is re-used, reprocessed or recycled but evidence suggests that the reprocessing of construction and demolition waste has increased steadily since 1990, putting the amount of reprocessed material at about 1 million tonnes a year.

In 1995, the Australian Federal Government has established through the Australian and New Zealand Environmental and Conservation Council (ANZECC) an Industry Waste Reduction Task Force. Construction and demolition waste was considered by the Task Force as a priority waste stream. The program was extended until 2001, ANZECC (2). In New South Wales, the Waste Minimisation and Management Act in 1995 has established a broad framework for the waste reform program. As a response to community request, a target of 60% reduction in waste disposal by the year 2000 has been specified. The construction and demolition waste has been identified as a priority for waste reduction as well.

A waste hierarchy has been established, recognising that avoidance is the best way to tackle the waste minimisation. The waste management hierarchy is Avoid (1), Re-use (2), Recycle-Reprocess (3), Disposal (4).

2. QUALITY OF RECYCLED MATERIALS

One of the major problems for the industry in utilising recycled construction or demolition materials is the fact that historically, the specifications for concrete, asphalt and pavement materials have been prescriptive, focussing on the raw materials properties rather than field performance, Dumitru (3).

There are few specifications for the use of recycled concrete in road constructions as a granular base and subbase material in NSW and Victoria.

Studies carried out by Bakoss (4) have indicated that there are several drawbacks of the recycled materials, namely:

- Variable nature of the recycled concrete aggregates in terms of grading and other specified properties.
- Recycled concrete aggregates do not always satisfy all of the current specification requirements.
- Recycled materials can contain a wide range of contaminants resulting in variability in their quality.

- Difficult to control the quality of recycled materials due to the variable nature of the feedstock.
- For economical reasons, the recycled concrete aggregates are used in large quantities as subbase materials even though not all the specification requirements are met.
- Depending on the resources and expertise of the producer, the quality and price of the recycled concrete vary.

2.1. Production and reprocessing

There are two major sorting techniques to remove the contaminants, reduce the variability and improve the quality of recycled materials.

i) Pre-crushing selections
ii) Post-crushing separation

A strict control on the level of contaminants during the pre-crushing selection will result in more consistent quality, better performance and hence better price for the materials.

Post-crushing separation method involving hand-sorting and removal of contaminants from the conveyor belt is not very practical. There are also some automated methods of sorting and cleaning the recycled materials Bakoss (4) which are grouped in three categories; electromagnetic separation, dry separation and wet separation.

One of the most efficient methods is the wet separation with the aquamator where the low-density contaminants are removed by water jets and a float-sink tank.

3. RECYCLED CONCRETE AGGREGATE CLASSIFICATION AND CURRENT USAGE

A classification of the recycled concrete aggregate in Australia was described by the University of Technology in Sydney, Bakoss (4).

Current applications of recycled concrete include bulk fill in landscaping and acoustic barriers, fill in drainage projects, production of low to medium grade concrete pavement and base and sub-base materials for road construction.

Due to current lack of adequate specifications for recycled materials and the differences between recycled and natural aggregates such as particle shape and texture, density, water absorption, durability, the introduction of recycled materials in other applications has advanced slowly, having only few examples of such applications.

4. DEVELOPMENT OF ECOLOGICALLY SUSTAINABLE CONCRETE AND ROAD PAVEMENT

The issues related to the ecologically sustainable concrete and road pavements, as presented in this paper, cover topics such as:

i) Recycled concrete aggregate (RCA)
ii) Recycled concrete washouts
iii) Reclaimed asphalt pavement (RAP
iv) Manufactured sands
v) Tunnelling materials
vi) Bottom ash and other similar products

4.1. Recycled Concrete Aggregate (RCA)

4.1.1 Recycled Concrete aggregates as natural aggregate replacement in concrete mixes.

Research carried out in Australia indicates that in general the recycled concrete can be used as natural aggregate in ready mixed concrete with potentially satisfactory performance for low grade concrete and for non-structural commercial concrete applications.

Sagoe-Crentsil (5) has demonstrated that marginal differences are in the compressive strength between the control mix using natural aggregates and RCA. Up to 10% reduction in strength characteristics have been observed. The major issue according to the same author is the elastic properties of RCA such as drying shrinkage and creep which are higher. For example, the drying shrinkage of RCA was in general about 150 μs higher compared with the control. Also, test results show about 10% difference in tensile properties between natural aggregates and RCA.

Successful attempts to utilise RCA as a commercial product in premixed concrete has been reported by Sautner (6).

In order to overcome some negative effects of RCA, some steps have been implemented, namely;

- The fine aggregate (-4.75mm fraction) was discarded.
- The recycled concrete aggregate was blended with 50% natural coarse aggregate.
- Fly ash and blast furnace slag has been added to the mix.

The results obtained show a lower strength for the RCA with a penalty of 10-15 kg of cementitious material and approximately 10% higher drying shrinkage.

Studies carried out by Boral Construction Materials and presented in Table 1 and 2, - Dumitru (3), cover two areas:

A. Assessment of total and partial replacement of natural sands with recycled concrete fines (-5mm).

The conclusions of the study where natural sands were replaced with recycled concrete fines were:

- The drop in the compressive strength is excessive.
- There is some increase in shrinkage.
- Bleeding is reduced with 25-50% of natural sand replacement which can be beneficial except under extreme hot weather when plastic cracking may occur.
- Water demand increases by approximately 4 kg/m^3 for each 25% increase in recycled concrete fines.
- The replacement of natural sands with recycled concrete fines decreases the concrete density.

Table 1

Replacement of natural sands with recycled concrete fines (-5mm).

Concrete Properties		Control	Percentage of replacement of natural sands			
		0%	25%	50%	75%	100%
Comp. Str. (MPa)	3 days	27	26	25	24	23
	28 days	45	43	40	39	37
Drying Shr. (με)	28 days	450	440	500	470	490
	56 days	580	570	640	630	650

B. Assessment of natural coarse aggregate replacement with recycled concrete aggregate

The conclusions of the study were that:

- The recycled concrete aggregate can be used in 20-40 MPa concrete mixes.
- There are penalties to be considered with regard to cement content, durability, permeability and drying shrinkage.
- There are no visual detrimental effects in concrete using RCA.
- The cement content penalty may be offset by lower cost of RCA.

Table 2

Replacement of natural coarse aggregate with recycled concrete aggregate.

Concrete Properties		Natural coarse and fine aggregate (control)	Natural aggregate but using 10mm RCA	10 and 20mm RCA	10 & 20mm RCA and 35% recycled concrete fines
Comp. Str. (MPa)	3 days	26	26	23	25
	28 days	45	41	39	41
Drying Shr. (µε)	21 days	390	420	500	510
	28 days	550	610	750	770

A study carried out by the University of Technology in Sydney – Bakoss (4) concluded that;

* 100% coarse aggregate replacement with recycled concrete aggregate produces drop in the compressive strength and modulus of elasticity and an increase in the drying shrinkage.

* There are some indications that variability in the properties of recycled concrete aggregate is not reflected proportionally in the properties of the concrete mixes produced with recycled concrete aggregates.

These conclusions are well in line with our finding and the differences in concrete mix characteristics are due to the fact that some of the recycled concrete aggregates are inferior to those of natural aggregates. These differences refer to lower particle density, higher porosity, higher water absorption and lower durability.

4.1.2 Recycled concrete aggregate as natural aggregate replacement in road pavements.

Some undesirable effects on compressive strength or increased cement content for a target strength when using recycled concrete aggregate in concrete mixes have conducted researchers to concentrate mainly in the utilisation of these materials in road pavements. In fact, this is an area where more emphasis is put on the field performance rather than raw materials properties.

There are several publications in Australia on this subject. Richardson (7) has carried out some laboratory studies concluding that:-

The recycled concrete aggregates are suitable for use as sub-base materials in road pavement.

- The gradings of the materials are within the local specification.
- Cement paste increases the moisture absorption and decrease the specific gravity.
- There is an increase in Maximum Dry Density and Optimum Moisture Content when compared with natural aggregates.

- There is an increase in the Los Angeles abrasion loss.

Also, Shayan (8) has concluded in his study that the recycled concrete aggregates perform well compared to natural aggregates in repeated triaxial loading, producing less permanent deformation and comparable resilient modulus. Also, the study concluded that cement treatment enhances the performance of the recycled concrete aggregates, meeting the requirement of 5000 MPa for estimated modulus of elasticity, recommended by Ausroads Pavement Design Guide.

Recycled concrete aggregates have been used to produce a base material to comply with the New South Wales Roads and Traffic Authority (RTA) Specification 3051 – Unbound and Modified Base and Sub-base materials for Surfaced Road Pavements, Dumitru (9).

The Dense Grade Base (DGB20) produced contained recycled concrete as coarse aggregate and due to the lack of fines, some quarry dust (-4.75 mm) was added to produce the final product.

The selection of the raw feed at the source and at the gate was very important and the demolition contractors were made aware that foreign materials in large quantities would lead to the outright rejection of the materials. Spotters at the gate were required to inspect each truck load for signs of unacceptable materials.

The material produced has been successfully used as a base material in one of the local council's roads in the Sydney metropolitan area. Its quality and workability characteristics were highly appreciated and the field performance after more than 3 years is excellent.

4.2. Recycled concrete washouts

One of the major problems facing the concrete industry has been that after making deliveries to job sites, the concrete mixers must be hosed out in order that all residue from the concrete mixture is removed. This is done to ensure that there is no contamination of subsequent loads of concrete, nor any hardening and setting within the inclined drum mixers which may result in reducing carrying capacity or impair the mixing efficiency. Other concrete which is placed in the washout pits is sourced from rejected deliveries which are returned from the site due to non-conforming quality or ordering more than required. Substantial amount of money are paid as tip fees to dispose of the material.

Following trial blends assessment, a combination of concrete washouts and picrite quarry dust was the most successful and an excellent sub-base or base material has been produced. The product, called 20mm Recycled Road Gravel, is durable, complies with grading requirements and has an excellent workability. Some of the product characteristics are presented in Table 3.

Table 3
20mm Recycled Road Gravel properties.

Product Properties	Results
Plasticity Index %	Nil
Moisture Content (MDCS) %	9.5
Dry Density at Compaction %	2.03
CBR at 2.5mm and 5.0mm Penetration %	60/80
Wet/Dry Strength Variation %	44

The product has been successfully used for a petrol station construction job, school playgrounds and parking areas, local council roads, access roads, as patching material in pot holes, trenches etc. Furthermore, savings from dumping fees have been achieved.

4.3. Reclaimed Asphalt Pavement (RAP)

4.3.1 Reclaimed Asphalt Pavement in road pavements

The Roads and Traffic Authority (RTA) of New South Wales has, for a number of years, successfully used up to 10% RAP in asphalt mix production. Based on a concept developed by the Danish Road Institute (10), laboratory and field trials have been carried out, Dumitru (11) using different blends of RAP and recycled crushed concrete as material for road pavements. The laboratory trials have concluded that:

- The particle size distribution of all these blends comply with the current RTA specification.
- Optimum Moisture Content (OMC) is lower as the proportion of RAP in each blend was increased. Overall the OMC has been found to be higher than for a conventional dense grade base (DGB20).
- The results for unconfined compressive strength show results ranging from 2.9 to 4.3 MPa, indicating that a greater compactive effort may be required in the field depending on bleed types.
- The durability of the blends are within the current specification for natural aggregates. The variable proportion of mortar in the recycled concrete aggregate may increase the wet/dry strength variation.
- The falling head permeability shows that the blends are more porous than the conventional DGB20 used as a control.
- Limited data on resilient modulus and permanent strain properties shows that the blend with lower RAP has similar resilient modulus compared to the control and permanent strain has increased with an increase in RAP content.
- The Modified Texas Triaxial strength and the California Bearing Ratio (CBR) show better results in the blends with lower RAP content.

Two field trials have been carried out so far under heavy vehicle loading. The first trial was located in a low lying area with the water table at the top of the sand subgrade. The pavement has been constructed on a heavily trafficked road at a hard rock quarry operation using a control mix (DGB20) and two RAP blends (low and medium level). There were no problems reported by the contractors with handling or compaction. The field trial sections were trafficked by the quarry highway fleet for two weeks prior to the asphalt being layed.

The construction of the trial has been monitored for deflection on a regular basis using the Benkleman Beam Apparatus with measurements taken at 5 metre intervals. From data available, all sections are performing well.

The second field trial finalised in October, 1999 has been carried out in a 600m section over a busy and heavy trafficked road (Figure 1). The contractor reported no problems with handling or compacting, the blends being supplied at an OMC through a pugmill. Some of the relative compaction figures varied between 101.0% to 107.5% depending on the type of blend used.

Figure 1. Field trial using low RAP/crushed concrete blends, a very homogeneous material with no signs of segregation.

The conclusion is that low proportions of RAP and high proportions of RCA can be blended to produce good quality roadbase. The blends can be treated as unbound material for the purpose of material characterisation for the determination of pavement design thickness.

4.3.2 Reclaimed Asphalt Pavements in concrete mixes

A series of trials have been carried out, Dumitru (2) to assess if RAP or bitumen coated aggregate produces a pavement concrete with an enhanced flexibility and a lower modulus of elasticity.

Some of the results are presented in Table 4 concluding that:

- Water demand has increased in the mixes with RAP but with no effect on air content.
- Bleeding was lower than in the control mixes.
- The compressive strength was lower, with an increase in drying shrinkage in RAP mixes.
- For a nominal mix of 7-10 MPa, the flexural strength has improved reducing the possibility of cracks at early age. Also, the modulus of elasticity was lower than the control. In situations where flexural strength and modulus of elasticity are more important than compressive strength, the incorporation of RAP in concrete mixes is of great interest.

Table 4
Effect of RAP on concrete mix properties.

Concrete mix properties		Type of aggregates Natural aggregates (control)	10mm RAP 20mm natural aggregates	20mm RAP 10mm natural aggregates	RAP Only
Comp. Str. (MPa)	3 days	5.8	6.5	5.6	4.0
	28 days	11.7	13.3	10.7	8.8
Flexural Str. (MPa)	3 days	0.9	1.7	1.6	1.2
	28 days	2.3	2.3	2.1	2.1
Modulus of Elasticity (X 10^4 MPa)	28 days	2.0	1.94	1.50	0.98
	56 days	2.2	2.14	1.61	1.24
Drying shrinkage ($\mu\varepsilon$)	21 days	470	450	560	680
	56 days	550	560	720	890

Trials with higher strength concrete (32MPa) using RAP indicated that there are strength losses, the losses against control varying between 46.3% at 7 days to 53.3% at 90 days.

4.4. Manufactured Sands

Regional and local natural sands shortages in Australia have encouraged an increased interest in the utilisation of quarry dust. The perception that all quarry dusts produced are waste is incorrect as quarry dust has been successfully used in asphaltic concrete, roadbase, masonry, premixed concrete, drainage fill, etc.

Studies carried out by Dumitru (12, 13, 14) have demonstrated that additional processing is required before quarry dust can be fully utilised as natural sand replacement.

Such additional processing is necessary as the shape in particular and the particle size distribution of quarry dust compares badly with the natural sands used in concrete mixes. Poor shape and problems related to size distribution may lead to poor workability and finishability, higher bleeding rates, plastic cracking and a poor in situ performance of concrete mixes.

The abovementioned studies have assessed the effects of Vertical Shaft Impactors (VSI) on shape and gradings, ways to assess the improvement in shape, conditions in which processed quarry dust (Manufactured Sands) can fully replace natural sand in concrete mixes without significant penalties. Issues such as abrasion and skid resistance, have also been considered.

The conclusions of these studies were that:

- There are benefits in using a VSI in processing quarry dust for basaltic rocks and crushed river gravel into Manufactured Sands. An increased amount of cubical material has been obtained as compared to the raw feed.
- A modified Cone Flow Test has been successfully used to assess particle shape and texture of the Manufactured Sands.
- Levels up to 15% of the -75μm fraction in Manufactured Sands can be acceptable and not detrimental to the plastic and hardened properties of the concrete mix.

- Conventional concrete mixes need some changes in the aggregate to sand ratio or admixture dosages in order to have the full benefits of the Manufactured Sands.
- Skid resistance and abrasion resistance of pavement concrete mixes using Manufactured Sands or quarry dust are as good if not better than when natural sands are being used. Some of the results presented in Figures 2a/2b and 3, are radically different than currently accepted views on this matter.
- Only unweathered and sound materials should be used for Manufactured Sand production, sourcing the materials only from well established sources of aggregates.

Only unweathered and sound materials should be used for Manufactured Sand production, sourcing the materials only from well established sources of aggregates.

Figure 2a Skid resistance of manufactured quarry fines

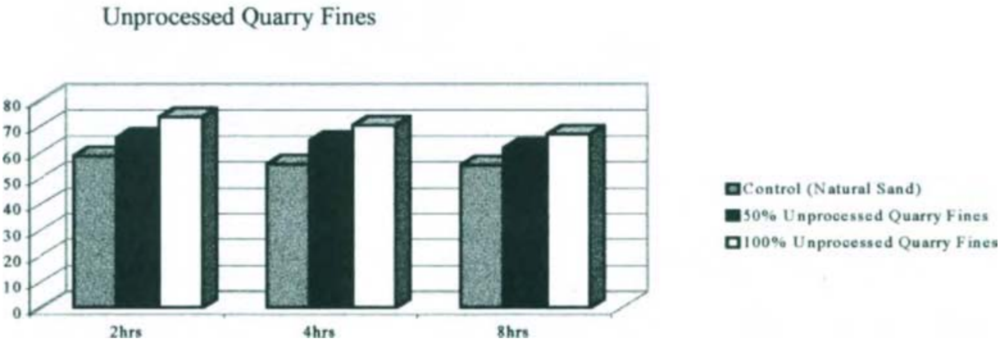

Figure 2b Skid resistance of unprocessed quarry fines

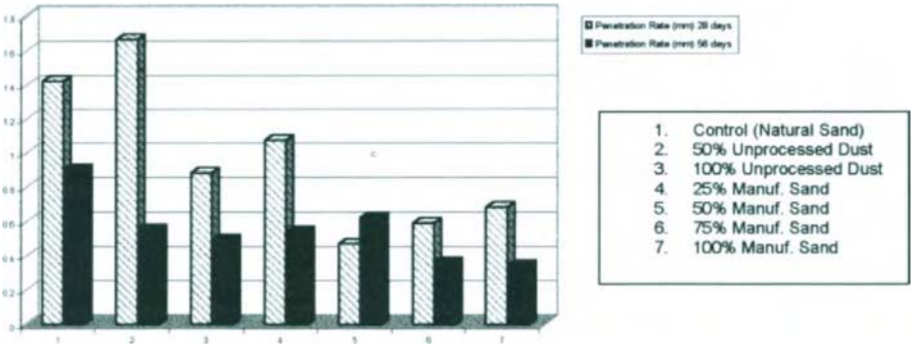

Figure 3 Chaplin Abrasion Resistance of Unprocessed and Manufactured Sands – Basalt

Recent work carried out on some ignimbrite rock has confirmed the previous results. Furthermore, some improvement in compressive strength has been observed together with excellent results on initial and final setting time.

4.5. Tunnelling materials

Work carried out in Sydney metropolitan area as a part of Olympics infrastructure has included a lot of tunnelling, with problems related to the disposal of the excavated materials, mostly fine dune sands and sandstones. Major projects such as City to Sydney Airport rail link, Eastern Distributor road link and more recently the M5 East road extension have produced large amounts of materials which, instead of being disposed of in land fills, have been or are to be reused in situ or elsewhere.

The contractors have been asked to establish strategies in order to minimise waste and the use of land disposal sites. The main strategy for the tunnelling work was to reuse some of the excavated materials on site, directing materials to another project after some reprocessing.

Most of the dune sand has been used as fine sand replacement in concrete mixes after washing in order to eliminate some excessive -75µm fraction. The sandstone has been crushed and has been used as a subbase material in a number of council roads or new housing developments.

More recently, following discussions with the Roads and Traffic Authority, a new selected fill has been successfully produced using sandstone and RAP blends. More work is in progress but some of the results presented in Table 5, indicate a good quality selected fill.

Table 5
Properties of selected fill using sandstone from tunnelling excavations and RAP

Selected fill characteristics	Before	After
	Pretreatment	
Liquid Limit %	Non plastic	20
Plasticity Index %	Non plastic	5
Maximum Dry Compressive Strength (MPa)	7.2	7.5
Moisture Content at MDCS (%)	10.0	12.0
Dry Density at MDCS (t/m^3)	2.07	2.01
CBR at 2.5mm/5.0mm Penetration %	60/60	20/25

4.6. Bottom ash and other similar products

The coal-burning residues from power-generation stations are known in the very fine size fractions as fly ash or as bottom ash as a coarser fraction. Fly ash is universally recognised as a pozzolanic material with some excellent results in controlling the ASR (alkali silica reaction).

Some work carried out by Dumitru (3) has identified a number of applications for bottom ash which include:

- Flowable fill or CLSM (controlled low strength material).
  With a proper mix design and adequate admixtures, a free flowing material has been produced, with self-levelling properties and minimal segregation. With a compressive strength ranging from as low as 0.5 MPa to 15 MPa or even higher, the material can be used as trench filling, backfilling, filling of large cavities in underground mining operations or as a blend in subbase material in pavements.
- Low strength permeable or drainage layer
  Some work is currently being undertaken to assess the good permeability of the bottom ash in a 5 MPa concrete mix for some subgrade applications. The problem that needs to be overcome is the fact that bottom ash has a low mechanical interlocking capacity.
- Rolled compacted concrete (RCC)
  Trials carried out show an improvement in the surface finish and compactivity for mixes using bottom ash. The pozzolanic nature of the bottom ash provides the ability to heal the microcracks and contributes to the long term gain in compressive strength.
- Kerb and gutter concrete
  A combination of bottom ash with 7 to 10mm coarse aggregates has improved the crack-resistance of the material.
- Structural concrete
  Trials carried out show that there is a 10% strength penalty when natural sands have been replaced with bottom ash in a concrete mix.

From data available it can be concluded that bottom ash is an attractive product. Transport cost and its availability on the market, balanced by some good engineering properties may decide on the end use and extent of utilisation of bottom ash.

5. SYDNEY 2000 OLYMPIC SITE - WASTE MINIMISATION INITIATIVES

The Olympic Co-ordinating Authority was one of the first to adopt uniform "green" specifications for construction of the Sydney 2000 Olympic Games venues. These specifications required adaptance of a strict energy management strategy along with material selection to minimise pollution, conserve resources and provide durability. The basic philosophy adopted was "reduce, re-use, recycle" which requires that the creation of waste be avoided or reduced at the point of generation, remaining waste should be re-used or recycled and disposal to landfill should be minimised. This philosophy presented a considerable challenge since the major site at Homebush Bay was previously an abattoir, a landfill site and a quarry and required major remediation.

The Olympic site in Sydney has been successfully used by EPA (1) as a good example of waste minimisation initiatives.

During site preparation, 200,000 tonnes of recycled concrete from the demolition of the old structures at the site have been used. Furthermore, 400,000m^3 of excavated earth has been used for landscaping of the site. On top of approximately $12 million savings due to lower cost of material, almost 600,000 tonnes of demolition and earthwork was diverted from landfill.

In the construction of the road infrastructure, large amounts of recycled construction and demolition materials were used, including 150 m^3 of concrete from excavation was crushed and re-used on site, 40,000 m^3 of sandstone from other construction areas was used as foundation materials for roads, 5,000t of quarry dust was used for pipes bedding, and 125,000t of crushed concrete has been used as base and subbase material.

Other initiatives involved the collection and re-use of stormwater for irrigation and dust suppression, and in structural concrete, blended cements have been used which contain high percentages of fly ash and blast furnace slag to minimise use of high energy consumption portland cement.

Numerous other initiatives of waste minimisation best practice are presented in the Olympic Co-ordination Authority's Compendium of ESD Initiatives and Outcomes for OCA Facilities and Venues, Volume 1 which sets out the Sydney 2000 Olympic "green" principles which are being used as a model for future specifications embracing best environmental practices.

6. CONCLUSIONS AND RECOMMENDATIONS

- Construction and demolition waste is a significant contributor of the solid waste stream.
- There are changes in the attitude to the utilisation of such material. Economical considerations are reconciled with an ecologically sustainable behaviour which together with tighter government controls on waste disposal will make re-use construction and demolition materials economically viable.
- The waste hierarchy Avoid (1), Re-use (2), Recycle/Reprocess (3), Disposal (4) recognises that avoidance is the best way to tackle the waste minimisation issue.
- The waste minimisation is not an environmental problem only, but a way to save the natural resources and energy as well.
- Several applications of using recycled materials, waste or by-products have been assessed. Some of these materials are now considered as premium ingredients by the concrete and road pavement industries.
- It is necessary to make some modifications to the current specifications in order to accommodate more recycled materials.
- New performance based specifications for materials incorporating construction and demolition waste are issues to be urgently considered.

- Amendments to current specifications or new performance based specifications should take into consideration some technical disadvantages, undesirable effects or penalties in conjunction with lower cost of recycled products and the challenges faced by the society in the 21st century.
- Further government/industry joint research is recommended to be undertaken, together with the preparation of a code of best practice for the recycled and waste industry.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

The use of reclaimed asphalt pavement (RAP) aggregates in concrete

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The paper presents a laboratory study on the properties of ordinary Portland cement (OPC) concrete made with reclaimed asphalt pavement (RAP) to substitute natural aggregate. RAP aggregates were incorporated in concrete on the basis of maximum packing of the particles to provide a mixture with minimum voids and thus optimum performance. Concretes were made with various combinations of natural and reclaimed aggregates. The resultant mixtures were:

a) control mixture using natural sand and natural gravel.
b) mixture containing reclaimed coarse aggregate and reclaimed fine aggregate.
c) mixture containing reclaimed coarse aggregate and natural sand.
d) mixture containing reclaimed coarse aggregate and natural sand where 30% of the ordinary Portland cement was substituted with fly ash (FA).

The weight composition and water/binder ratio was the same for all the mixtures. The results of the study show that RAP aggregates reduce the compressive and tensile strength of concrete and that the reduction is proportional to the percentage of RAP used. Fine and coarse RAP cause more reduction than coarse RAP and sand. Of the mixtures containing RAP, the use of coarse RAP aggregate with OPC or OPC+FA did not affect the engineering properties of concrete, however, the performance properties were much improved with the use of fly ash as indicated by the measurements of porosity and permeability. The RAP concrete mixtures exhibited enhanced ductility and high strain capacity when compared to the control concrete mixture. These improved properties can be useful for the use of RAP aggregate concrete in the construction of road bases and sub-bases. The material is also potentially of use for all non-structural purposes.

1. INTRODUCTION

This investigation deals with the use of reclaimed asphalt pavement (RAP) aggregates in ordinary Portland cement concrete particularly for the construction of road pavements. Concrete mixtures consume large amounts of natural aggregates which account for more than 70% of their total volume. In recent years the demand of quality natural aggregates has increased rapidly and environmental pressures, combined with the landfill tax, have led to the consideration of using RAP aggregates in structural concrete as well as road application. In many cases quality aggregate is simply not available or is economically unable to be accessed. Therefore there exists the need to look into alternatives that will provide suitable aggregate for concrete construction.

Recycled aggregate is produced in large quantities during the process of maintaining or demolishing existing Portland cement concrete, asphaltic concrete (AC) and masonry structures. Hansen [1] indicated that the US generates 60 million tons of demolition wastes per year. In comparison, the UK accounts for 11 million tons of waste, 50 million tons in European countries, and 12 million tons in Japan. Waste and recycled materials account for about 10% of the aggregates used in the UK, and it is government policy to increase the usage of recycled materials in the interest of conservation of material resources and environmental protection [2].

Currently the main markets for recycled aggregates are as materials for landfills and sub-base layers in construction. According to Collins [2], up to 40% of the demolition wastes in the UK are recycled, however, they are only used in such low-grade applications. The lack of usage in high-grade application may be due to the inadequacy of Standards giving specifications for the use of recycled aggregate, which in turn discourage the construction industry of using recycled aggregates in higher grade applications, such as concrete. The main UK specification for concrete aggregates is BS 882 [3], which deals strictly with natural aggregates and therefore excludes demolition waste.

Reclaimed asphalt pavement (RAP) aggregates are produced primarily as a result of preparing existing asphaltic concrete (AC) pavements for repaving or rehabilitation to correct deficiencies such as rutting, cracking and stripping. The common uses of RAP is in hot and cold bituminous mixtures, however, very little information is available regarding its use as an aggregate in ordinary Portland cement (OPC) concrete. This paper presents an initial investigation on selected engineering properties and performance of concrete made with RAP aggregates.

2. MATERIALS AND CONCRETE MIXTURES

The cement used in this investigation OPC supplied by Castle Cement, UK and complied with the requirements of BS 12 [4]. The fly ash (FA) was obtained from Drax Power station in Yorkshire and conformed to BS 3892 [5]. Quartzitic sand and gravel were used as natural aggregates. The sand grading was medium (zone M) and the gravel had a maximum nominal size of 14 mm, both conformed to BS 882 [3]. RAP aggregate was obtained from Tilcon North while they were reconstructing a road section in Newcastle-upon-Tyne. Table 1 gives the measured physical properties of the natural and RAP aggregates.

Table 1. Physical properties of the aggregates used in this study

Aggregate	Gravel	Sand	Coarse RAP	Fine RAP
Specific gravity	2.68	2.73	2.56	2.41
Moisture content (%)	0.10	0.06	0.23	0.44

The control concrete mixture (OPC: sand: gravel) was proportioned on the basis of maximum packing of the particles with minimum porosity following the procedure proposed by Cabrera and described in reference [6]. Due to the unknown packing properties of the RAP aggregates in concrete mixtures, fine and coarse RAP were proportioned in different ratios to obtain a minimum porosity mixture and thus with optimum performance. Figure 1 shows the porosity results for the RAP fine and coarse aggregate mixtures, while the optimum mixture of RAP coarse aggregate with cement/sand (mortar) is shown in Figure 2.

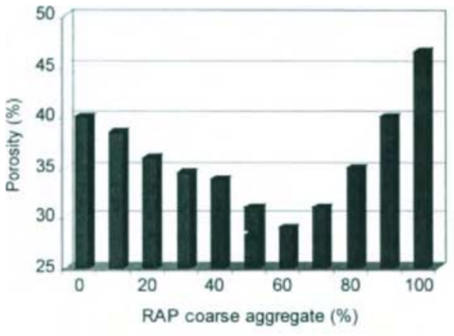

Figure 1. RAP coarse to fine aggregate mixture proportion

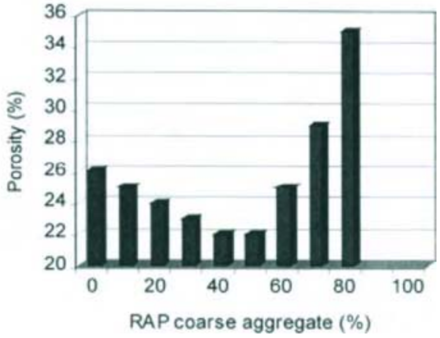

Figure 2. Coarse RAP to cement/sand (mortar) mixture proportion

Four concrete mixtures were made for this study. The first mixture contained RAP as both fine and coarse aggregates with OPC binder. The second contained RAP coarse aggregate and OPC/sand mortar. The third mixture was the same composition as mixtures 2 but with 30% of FA replacing OPC. The control mixture was made from OPC with natural quartzitic sand and gravel aggregates. The amount of mixing water was maintained constant for all the mixtures to give a water/binder ratio of 0.5. In order to improve the workability of the concrete mixtures, a dosage (1%) of superplasticizer was used. Details of the different mixture proportions are given in Table 2.

Table2. Composition of the concrete mixtures used (kg/m^3)

Mixture	**OPC**	**FA**	**Sand**	**Gravel**	**RAP [F]**	**RAP [C]**	**Water**	**SP (l/m^3)**
RAP (F+C)	325	-	-	-	760	1140	160	3.25
RAP ©	325	-	760	-	-	1140	160	3.25
FA/RAP ©	227	98	760	-	-	1140	160	3.25
Control	325	-	760	1140	-	-	160	3.25

3. METHODS OF TESTING

After casting and compaction, the concrete specimens were left overnight in the laboratory. On the second day, the specimens were de-moulded and cured in a fog room maintained at 20°C and 99% relative humidity for 3, 7 and 28 days before testing.

3.1 Compressive strength

The compressive strength test was carried out on 100 mm cubes following the procedure described in BS 1881: part 116 [7].

3.2 Flexural strength and toughness

Concrete prisms (100×100×500 mm) were used for the measurements of flexure strength in accordance with BS 1881: Part 118 [8]. The prisms were simply supported and loaded with symmetrically two-point loading (at third points of the loaded span). The load was increased gradually with continuous monitoring of the mid-span deflection until failure.

3.3 Porosity

The vacuum saturation apparatus was used for the determination of the total porosity using water as a replacement media. Concrete slabs were prepared as explained above and cores (50 mm diameter and 40 mm height) were drilled at the different testing ages. The apparatus and test procedure are described in reference [9].

3.4 Permeability

The transport properties of concrete are of great importance with regard to its performance, as they describe the continuity of pore structure and therefore the resistance to the penetration of harmful substances into concrete. In this study, concrete cores of (50 mm diameter and 40 mm height) were obtained from the different concrete mixtures and dried to constant weight in an oven at 105±5°C before testing. The measurement of oxygen permeability was carried out using the Leeds Permeameter Cell as described by Cabrera and Hassan [10].

4. PRESENTATION OF RESULTS AND DISCUSSION

4.1 Compressive strength

The compressive strength results of the control and the RAP concrete mixtures are presented in Figure 3. The results show that the use of RAP aggregate reduces the compressive strength of concrete. The strength behaviour of the RAP (C) was quite similar to that of the FA/RAP (C) indicating no improvement with the use of fly ash with coarse aggregate RAP. Both concrete mixtures showed a reduction in strength of about 65% at the age of 28 days when compared to the control mixture. The lowest strength values at the different testing ages were obtained for the mixture containing fine and coarse RAP, which exhibited a strength reduction of 80%. These findings are in agreement with Delwar et al. [11] who reported that the compressive strength of concrete decreases as the percentage of the RAP aggregate increases in the mixture.

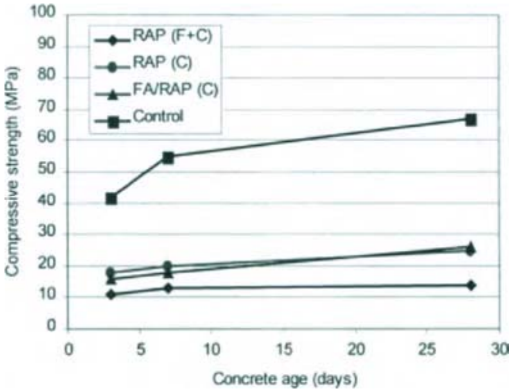

Figure 3. The compressive strength of the control and the RAP concrete mixtures at different ages

It is important to highlight here that different modes of failure were observed for the different concrete mixtures. Whilst the control concrete specimens crushed under the failure load showing clearly brittle failure, the RAP concrete specimens, especially the one incorporating fine and coarse aggregates, deformed but did not exhibit cracks at failure.

The compressive strength of the RAP concretes used in this investigation are less than the Department of Transport's requirement, viz. 31 MPa at 7 days and 44 MPa at 28 days. However, it seems likely that a lower replacement level of RAP would allow the strength specification to be met.

4.2 Flexural strength

The results of the flexure test carried out at the age of 28 days for the different concrete mixtures are shown in Figure 4. Similar to the compressive strength results, the maximum flexure load was obtained for the control concrete mixture. Both OPC and FA concrete mixtures containing coarse RAP aggregate, RAP (C) and FA/RAP (C), showed identical behaviour with about 35% reduction of the flexure strength when compared to the control concrete. More reduction of the flexure strength (about 45%) was found with the concrete mixture RAP (F+C) containing fine and coarse RAP aggregates.

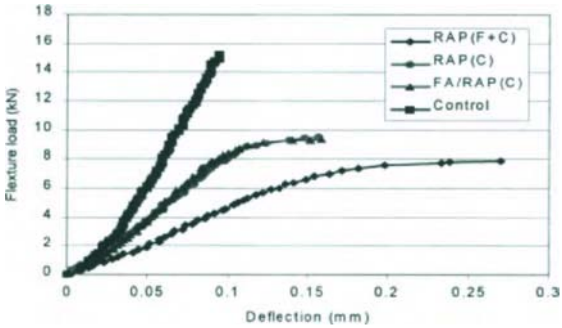

Figure 4. Flexure load-deformation curves for the different concrete mixtures

Figure 4 shows also the mid-span deflection measured under flexure load until failure. Again it can be seen that the nature of failure of the control concrete was more abrupt and explosive at crack initiation than of the mixtures containing RAP. The slope of the load-deflection curves for the RAP concrete mixtures indicates lower modulus of elasticity values and hence more ability to deform under load application. The crest curvature occurs after the elastic limit shows that RAP aggregate absorbs loading better that natural aggregate in concrete mixtures. These advantages of improved deformation and ductility properties suggest the use of RAP in concrete subjected to impact and cyclic loads, although the test conditions did not reflect those in service where there are higher rates of loading and seasonal high temperatures. Both those factors affect the modulus of elasticity, and not necessarily to the same extent for the control concrete and RAP concretes.

The performance-related properties of concrete based on the pore structure and transport properties are presented in the following sections.

4.3 Porosity

The porosity values obtained for the four concrete mixtures at different ages are shown in Figure 5. Whilst the control mixture showed lower porosity values than the RAP concrete mixtures, the difference was not as much as that shown by the strength results. The highest porosity values were obtained for the RAP (F+C) concrete mixture, which are about 20% higher then the control mixture at the different tested ages.

The results also show the general trends of decreasing porosity with age for all mixtures. OPC concrete mixtures showed almost similar reduction rate whereas the porosity of the fly ash concrete mixture decreased more rapidly with time, so much so that at 28 days it had a porosity value only 5% greater than the control mixture. This indicates the beneficial use of fly ash which improves the packing capacity of concrete materials and reduces the average pore diameter.

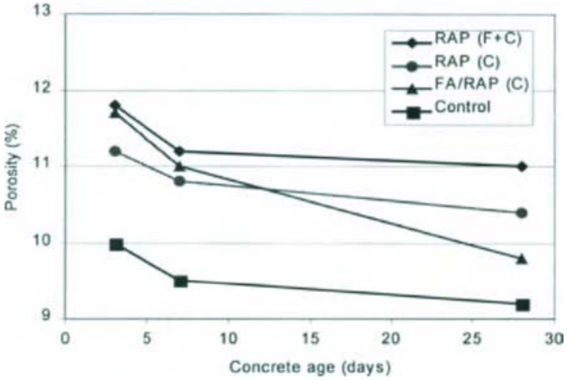

Figure 5. Reduction of porosity with age for the control and RAP concrete mixtures

4.4 Oxygen permeability

Figure 6 shows the oxygen permeability for the control and RAP concrete mixtures. The results indicate similar trends to the porosity results but with larger differences. The permeability values of the RAP (F+C) and RAP (C) concrete mixtures were high at 3 days of age and decreased with time. However, they still had relatively high values at 28 days when compared to the control concrete mixture.

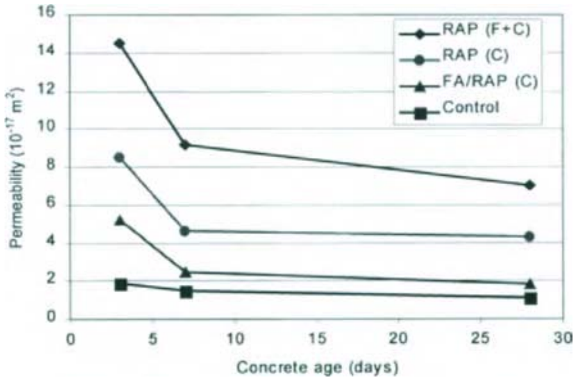

Figure 6. Variation of oxygen permeability with concrete age

Fly ash shows again a significant effect on the permeability of concrete containing RAP aggregate as shown in Figure 6. At 28 days the FA/RAP (C) had a permeability value quite similar to that of the control concrete, which is considerably less that the values for other RAP concrete mixtures. These results, coupled with the porosity results, indicate that the addition of fly ash has a positive effect on the performance properties of concrete. The volume and continuity of the pores within concrete were greatly reduced. Wainwright et al. [12] also found that the use of fly ash had a positive effect on the properties of recycled aggregate concrete.

In general the results of this study show that the use of RAP as an aggregate in concrete reduces the strength properties of concrete but improves its ductility. Also the performance-related properties of RAP concrete can be much improved with the use of fly ash as partial replacement of OPC. These advantageous allow the use of the large quantities of RAP to substitute natural aggregate in concrete applications where low-strength and high shock absorbent properties are required.

5 CONCLUSIONS

1. The use of RAP reduces the strength properties of concrete, but improves its strain capacity and shock absorbent properties.
2. Fly ash improves the microstructure and transport properties of concrete, these improvements were not detected by the strength properties.
3. RAP concrete mixtures exhibited satisfactory strength properties allowing them for use in low-strength and high ductility applications.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Preliminary laboratory investigation of thermally treated recycled concrete aggregate for general use in concrete

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This paper deals with a preliminary laboratory study to assess the effectiveness of thermal treatment methods to improve the quality of recycled concrete aggregate. The samples used for the study consisted of sieved fractions of crushed concrete that were subjected to various thermal treatments at temperatures of either 650 °C or 800 °C. In each case, the treatment lasted for a period of 0.5 or 1 hour. After the thermal treatments, the samples were first investigated by means of polarising and fluorescence microscopy followed by strength tests on mortar and concrete specimens prepared with one of the treated samples. The thermal treatments caused considerable reduction in the amount of cement paste or mortar adhering to both the fine and the coarse aggregate particles. The reduction was more pronounced in the case of the samples treated at a temperature of 800 °C than those treated at 650 °C. The integrity of the aggregate particles was found to a large extent to be preserved. The strength development of mortar and concrete specimens, prepared with one of the treated samples was slower than that of conventional river-dredged aggregate but reasonably good. Although this is a preliminary study, the results indicate that thermal treatment of recycled concrete aggregate at a temperature of about 800 °C can yield good quality aggregates, with properties which are reasonably comparable to conventionally used river-dredged aggregates.

1 INTRODUCTION

In the Netherlands, owing to the damage caused to the environment from continuous dredging of riverbeds for good quality aggregates, the government has adopted a policy to support innovative programmes that will promote reuse of recycled concrete aggregate and limit further dredging of riverbeds. This policy calls for broadening of the current spectrum of application of recycled concrete aggregate. Other areas of application of recycled concrete aggregate than the present use in relatively low-quality concrete (as partial replacement of the coarse aggregate fraction) need to be explored. At the moment the bulk of recycled aggregates (mixed recycled concrete and masonry) is found in relatively low technical applications such as sub-bases for roads (road foundations) and embankments. The possibility of utilising both the coarse and the fine fractions of recycled concrete aggregate to produce high quality concrete needs to be examined. This is not only important from the point of view of materials use but, also important in order to 'close the concrete loop' – from reuse to recycling [1].

One of the main reasons why recycled concrete aggregate is not attractive for use in producing high quality concrete is the difficulty associated with mixing of such concrete. In general, this difficulty arises from the high water demand of recycled concrete aggregate caused by residues of cement paste or mortar adhered to the aggregate particles after processing of the concrete rubble. This effect is of course more important for the fine materials (fine fraction) than for the coarse fraction.

Another reason for the lack of interest in recycled concrete aggregate is the lower strength development of concrete mixes prepared with such aggregate compared to conventional aggregates. This arises from the fact that, in most cases the cement grains in these residues had already undergone complete hydration and therefore do not contribute significantly to the strength development of the new concrete. The extra cement paste (very often with relatively high water-cement ratios) also poses uncertainties regarding durability.

These two aspects show that residues of cement paste or mortar adhering to the aggregate particles pose a major problem with regard to use of recycled concrete aggregate. It is therefore of great importance that any research programme, designed to improve the quality of recycled concrete aggregate for general use in concrete be first and foremost geared towards removing a significant amount of these residues from the aggregate particles.

An additional "problem" is that at the moment only 20 % by volume of recycled concrete aggregate can be applied in new concrete without further changes or modification structural analysis. Application of more than this allowable amount requires further investigation. In most cases this creates logistical problems – there must be more coarse aggregate types at the concrete production centres in order to counteract these unexpected problems.

In 1998, a research project was initiated by TNO to address this issue. Initial phases of this research project have been concentrated on the effect of thermal treatment on the integrity of the aggregate particles and the extent of separation of the cement paste and mortar from the aggregate particles.

In a pilot study, recycled concrete aggregate was heated in a laboratory oven at a temperature of 650 °C for duration periods of either 5 or 25 minutes. In that study, the integrity of most of the aggregate particles was preserved but a considerable fraction of the cement paste and mortar remained attached to the aggregate particles (20-40 % for the coarse fraction and more than 80 % in the fine fraction [2]). It was therefore decided to carry out the same treatment process at a higher temperature and for longer duration periods than in the case of the pilot study.

This paper summarises the results of a preliminary research project to assess the effectiveness of a number of thermal treatment processes to improve the quality of concrete recycled aggregate. The study reported here consisted of laboratory-based thermal treatment of crushed concrete aggregate, examination of the treated aggregates by means of optical microscopy and technological tests on concrete prepared with one of the treated aggregates.

2 EXPERIMENTAL

2.1 Samples

The samples used for the study consisted originally of crushed concrete aggregate of various particle sizes, obtained by crushing laboratory-made concrete cubes. The original crushed samples consisted of various particle sizes with a maximum particle size of about 16 mm. Another sample, consisting of crushed concrete aggregate but not thermally treated was used as reference. This sample had the same particle size as the thermally treated samples.

2.2 Experimental procedures

2.2.1 General

The tests carried out in this study consisted of the following:

- thermal treatment of crushed concrete aggregate with the aim of separating the cement paste from the aggregate particles
- examination of the treated aggregates by means of optical microscopy in order to determine the effectiveness of the treatment method, and
- technological and strength tests on concrete specimens prepared with one of the treated aggregates in order to assess any improvements in the quality of that recycled aggregate.

2.2.2 Thermal treatment of recycled concrete aggregate

The crushed concrete aggregate samples were separately heated in a laboratory oven at various temperatures for various duration periods as summarised in Table 1. A detailed description of the procedures used is given in [2].

After the thermal treatment, the samples were allowed to cool slowly at room temperature and finally sieved into two size fractions of 2-4 mm and 4-8 mm as shown in Table 1.

Table 1
Information regarding the method of treatment of the recycled concrete aggregate.

Sample	Fraction	Description of the thermal treatment process (heating process) imposed on the recycled concrete aggregate
0	4 – 8 2 – 4	Untreated recycled concrete aggregate (reference material)
1	4 – 8 2 – 4	1 h at 200 °C, 1 h at 400 °C, 1 h at 600 °C, 1 h at 650 °C;
2	4 – 8 2 – 4	0.5 h at 200 °C, 0.5 h at 400 °C, 0.5 h at 600 °C, 0.5 h at 800 °C;
3	4 – 8 2 – 4	1 h at 200 °C, 1 h at 400 °C, 1 h at 600 °C, 1 h at 800 °C;
4	4 – 8 2 – 4	2 hours in a preheated oven at 800 °C

Samples 1, 2 and 3 were produced by placing the material in a cold oven, which were thereafter heated in steps. The idea behind this was that by heating in steps, the thermal stresses developed in the particles would be reduced. Sample 4 was produced by placing the material in a preheated oven at a temperature of 800 °C. As such, the thermal stresses developed in that sample would have been higher than the other samples. The duration periods for heating were chosen on the basis of heat of conduction calculations.

In the work described in [2], each of the two fractions was examined separately. From that study the effects of the thermal treatment were found to be similar for both fractions. As such, in this presentation, unless otherwise stated these two fractions shall be treated as one.

2.2.3 Optical microscopy

The purpose of the optical microscopical study was twofold. Firstly, it was performed in order to assess the effectiveness of the treatment method (that is whether the treatment processes have affected the integrity of the aggregate particles), and to determine the improvement in the quality of the resulting aggregate.

The preservation of the *integrity of the particles* was evaluated on the basis of the extent of microcracking of the particles. The *improvement in the quality of the aggregate* was assessed on the basis of the reduction in the amount of cement paste and mortar adhering to the aggregate particles after the thermal treatment process. The latter was supported by concrete technological tests on concrete mixes.

The thin sections were prepared by first mixing a representative sub-sample of each sample in a small plastic container with an epoxy resin containing a fluorescent dye.

After hardening, two small rectangular blocks were sawn from each specimen, separately glued to object glasses and impregnated under vacuum at about 40 °C with an epoxy resin containing a fluorescent dye. Thereafter two thin sections, each with a surface area of about 50 mm x 30 mm and a thickness of 20-30 Fm were prepared from each block for the thin section analysis.

Impregnation of the blocks with a fluorescent resin in this way makes it possible to study the thin sections by means of transmitted light and fluorescence microscopy.

By means of transmitted light microscopy, the mineralogical composition of the recycled concrete aggregate samples can be determined.

The fluorescent microscopy allows the porosity of the particles to be studied and to determine the extent of microcracking of the particles. The amount of cement paste or mortar adhering to the aggregate particles was determined with the aid of a "point-counter" attached to the microscope. A detailed description of this technique is given in Heijnen and Larbi [4].

2.2.4 Strength tests

The purpose of these tests was to compare the compressive strength of concrete specimens prepared with one of the treated concrete aggregates, "Sample 4" (see Table1) to those of concrete prepared with traditionally used river aggregates (river gravel and sand).

Using the coarse fraction (4-8 mm) of the recycled concrete aggregate and river-dredged sand, in combination with CEM I 32.5R, concrete specimens measuring 100 mm x 100 mm x 100 mm were cast into steel moulds. Thereafter, they were adequately compacted, covered with a plastic sheet and stored overnight in a fog room maintained at 20±2 °C. At the required time the specimens were subjected to compressive strength tests. Additional information regarding the concrete is presented with the test results in Table 5.

3 RESULTS AND DISCUSSION

3.1 Optical microscopy

The results of the PFM-analysis regarding the mineralogical composition of the samples and the "point-counting" analysis to determine the amount of residues of cement paste and mortar adhering to the aggregate particles is presented in the following sections.

3.1.1 Mineralogical composition and integrity of the treated concrete aggregate

Both the coarse and the fine aggregate fractions were river-dredged consisting essentially of rounded particles of sericitic sandstone, quartzite, porous and non-porous chert and fragments of limestone, feldspar, mica, calcite and oxides. None of the particles was found to show any form of physical degradation or chemical attack, for example from alkali-silica reaction.

The cement used in the cement paste or mortar was mostly ordinary portland cement, but some particles contained also blast furnace slag cement or portland fly ash cement. Almost all the cement and mortar attached to the aggregate particles had completely carbonated.

The extent of preservation of the integrity of the particles was evaluated on the basis of the average intensity of microcracking of the particles. Comparisons were then made for the samples per method of treatment. In performing this analysis, special attention was paid to the variation of microcracks among the particles for a particular treatment method using a comparable, untreated river sand or gravel as a reference sample. The criteria used for classifying the extent of microcracking in the particles are given in Table 2.

Table 2
Criteria used for classifying the extent of microcracking of the treated concrete aggregate.

Classification of the Extent of microcracking	Description of classification
Very low	20 % or less of the aggregate particles in the specimen contained more than 5 microcracks
Low	20-40 % or less of the aggregate particles in the specimen contained more than 5 microcracks
Moderate	40-60 % or less of the aggregate particles in the specimen contained more than 5 microcracks
High	60-80 % or less of the aggregate particles in the specimen contained more than 5 microcracks
Very high	80 % or more of the aggregate particles in the specimen contained more than 5 microcracks

Since almost each aggregate particle contained microcracks, the classification was based on particles containing 5 or more microcracks. The length of the microcracks was not considered in this analysis. All the microcracks considered had crack-widths of 10 μm or less. An overview of the average intensity of microcracking in the particles of each treated sample is presented in Table 3.

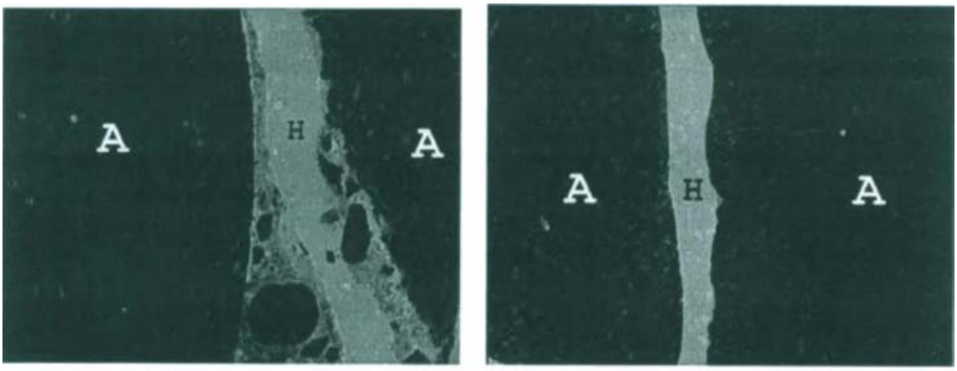
Table 3
Overview of the average intensity of microcracking in the aggregate particles of samples examined.

Sample	Fraction	Description of the thermal treatment process (heating process)	Intensity of microcracking
0	4 – 8 2 – 4	Untreated recycled concrete aggregate (reference material)	Very low
1	4 – 8 2 – 4	1 h at 200 °C, 1 h at 400 °C, 1 h at 600 °C, 1 h at 650 °C;	Low
2	4 – 8 2 – 4	0.5 h at 200 °C, 0.5 h at 400 °C, 0.5 h at 600 °C, 0.5 h at 800 °C;	Very low
3	4 – 8 2 – 4	1 h at 200 °C, 1 h at 400 °C, 1 h at 600 °C, 1 h at 800 °C;	Low
4	4 – 8 2 – 4	2 hours in a preheated oven at 800 °C	Very low

Figure 1 is a PFM-micrograph showing the intensity of microcracking in the aggregate particles of the reference sample and of Sample 4. The micrographs hardly show any microcracks in the aggregate particles in the two samples, although Sample 4 has been subjected to thermal treatment.

3.1.2 Amount of cement paste or mortar adhering to aggregate particles

The amount of cement paste or mortar adhering to the aggregate particles after the thermal treatment process is presented in Table 4. The amount of cement paste or mortar adhering to the aggregate particles was determined by means of "point-counting". All the treated samples show considerable decrease in the amount of cement paste and mortar residues that remain attached to the aggregate particles compared to the reference sample.



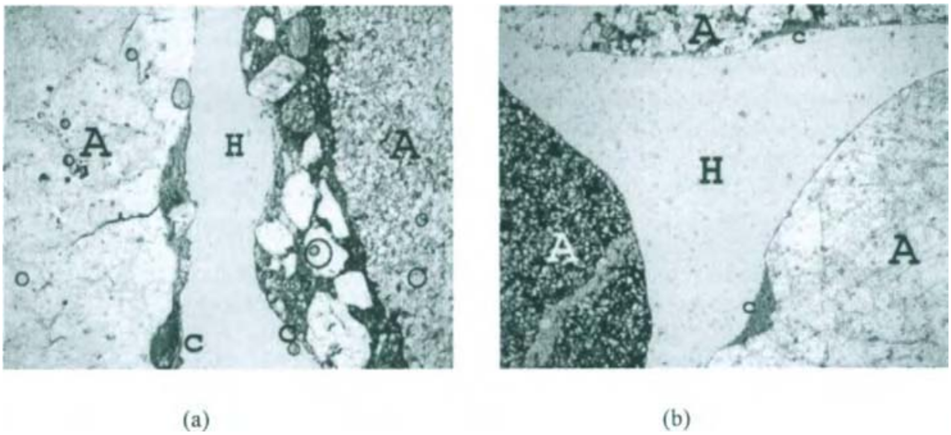
(a) (b)

Figure 1. PFM-micrograph showing the intensity of microcracking of the coarse aggregate particles in the reference sample (a) and Sample 4 (b). A = aggregate; H = fluorescent resin. Size of micrograph is 5.4 mm x 3.5 mm.

Table 4
Overview of the amount of cement paste or mortar left adhering to the aggregate particles of the samples examined.

Sample	Fraction	Description of the thermal treatment process (heating process)	Amount of cement paste or mortar adhering to particles
0	4 – 8 2 – 4	Untreated recycled concrete aggregate (reference material)	55
1	4 – 8 2 – 4	1 h at 200 °C, 1 h at 400 °C, 1 h at 600 °C, 1 h at 650 °C;	20
2	4 – 8 2 – 4	0.5 h at 200 °C, 0.5 h at 400 °C, 0.5 h at 600 °C, 0.5 h at 800 °C;	5
3	4 – 8 2 – 4	1 h at 200 °C, 1 h at 400 °C, 1 h at 600 °C, 1 h at 800 °C;	10
4	4 – 8 2 – 4	2 hours in a preheated oven at 800 °C	5

Figure 2 shows an overview of the amount of cement paste or mortar attached to the aggregate particles in the reference sample and in Sample 4. The particles in the treated sample contain a smaller amount of cement paste or mortar residues compared to the reference sample (see also Figure 1). In each thin section examined, there were small variations in the amount of cement paste or mortar residues attached to the aggregate particles but these minor variations are normally taken into consideration in the 'point-counting' analysis.



(a) (b)

Figure 2. PFM-micrograph showing overview of the amount of cement paste or mortar attached to the aggregate particles in the reference sample (a) and Sample 4 (b). A = aggregate; C = cement paste; H = fluorescent resin. Size of micrograph is 5.4 mm x 3.5 mm.

3.1.3 Evaluation of the results of optical microscopy

From the results of the optical microscopical analysis presented in Tables 3 and 4, the following deductions can be made:

1. Regardless of the aggregate fraction used, thermal treatment of crushed concrete (recycled concrete aggregate) in one-step from room temperature of about 20 °C to a temperature of 800 °C (*Treatment 4*) does not result in microcracking of the aggregate particles. The integrity of the particles is preserved. There is also excellent separation of the cement paste and mortar from the aggregate particles. In this case, the thermal treatment method applied can be classified as very effective.
2. Stepwise thermal treatment of recycled concrete aggregate, for relatively short duration periods from room temperature of about 20 °C up to a temperature of 800 °C (*Treatment 2*) does not result in microcracking of the aggregate particles regardless of the aggregate fraction used. The treatment method has hardly any effect on the integrity of the aggregate particles. The method also allows excellent separation of the cement paste or mortar from the aggregate particles. As such, this thermal treatment method can also be classified as very effective.
3. Stepwise thermal treatment of recycled concrete aggregate from room temperature of about 20 °C up to a temperature of 800 °C (*Treatment 3*) also gives reasonably good results regardless of the aggregate fraction used. For that matter, the effectiveness of this treatment method can be classified as good.
4. Stepwise thermal treatment of recycled concrete aggregate, for relatively short duration periods from room temperature of about 20 °C up to a temperature of 650 °C (*Treatment 1*) also gives reasonably good results with regard to microcracking of the aggregate particles, regardless of the aggregate fraction used. The method is, however, not effective in separating the cement paste or mortar from the aggregate particles, regardless of the aggregate fraction used. On this basis, the method of treatment may be classified as moderately good.

The results in Tables 3 and 4 show that heating of the recycled aggregate up to a maximum temperature of about 800 °C is necessary in order to achieve excellent or total removal of the cement paste and mortar from the aggregate particles. The results also show that stepwise heating for relatively short duration up to a maximum temperature of about 800 °C can achieve the same results as one-step heating from room temperature of about 20 °C to a maximum temperature of 800 °C. This means that instead of stepwise heating, it may be easier or more appropriate to heat the starting material (recycled concrete aggregate) in one-step from room temperature up to temperature of 800 °C.

3.2 Strength tests

An overview of information regarding the concrete compositions and the results of the strength tests are presented in Table 5. The mixes were adjusted to have similar workability by adjusting the water content.

The purpose of this test was to explore whether substitution of river gravel (4-8 mm) with 'thermally treated recycled concrete aggregate' (4-8 mm; Sample 4) in concrete will yield similar strength results. An overview of test results on the two concrete mixes is presented in Table 5.

Table 5
Information regarding the concrete specimens and results of the concrete strength tests.

Composition* and property	Mix A	Mix B
River gravel (4-8 mm)	1137	-
Thermally treated recycled concrete aggregate (4-8 mm)	-	1116
River sand (0-4 mm)	758	789
Cement, CEM I 32.5R	319	312
Water	166	163
Water-cement ratio	0.52	0.52
Average bulk density of 3 specimens (kg/m^3)		
after 1 day	2380	2380
after 28 days	2390	2390
Average compressive strength after 28 days (Mpa)	42	36

** all data in kg/m^3 n.d. = not determined

From the test, the following deductions can be made:

- the workability of both mixes was not determined but from visual examination was quite comparable;
- the average bulk density values of the two mixes after 1-day and after 28-day hardening periods were the same;
- the 28-day compressive strength of the concrete prepared with thermally treated recycled concrete aggregate was 14 % less than that of the river gravel-concrete (the reference concrete).

The reason for this lower strength development is not clearly known. Most likely it is caused by the remnants of cement paste and mortar adhering to some of the aggregate particles (the small amount of cement paste still remaining adhered to the aggregate particles). This anomaly calls for further investigation of other mixes, for example with different water-cement ratios, cement types and cement contents.

In a previous study [5], the density of microcracks in similar coarse aggregate particles of a recycled aggregate (used to prepare concrete) was found to be low. The recycled concrete aggregate, in that case, was not thermally treated. The homogeneity of the cement paste and the extent of bonding of the cement paste to the aggregate particles were also found to be good. In that concrete, a relatively high water content was used (a high water-cement ratio of about 0.55) in order to achieve the same workability as the reference concrete prepared with conventionally used river gravel. Even though in that concrete, only 50 % of the coarse aggregate was made up of untreated recycled concrete aggregate, a water-cement ratio of 0.55 was necessary in order to offset the high water demand of that fraction of recycled concrete aggregate. A most likely explanation for this is the high water absorption of the cement paste and mortar residues adhering to those aggregate particles. The results of the strength tests in that study were much lower than those obtained for concrete containing river gravel.

The present investigation shows that even lower water content (a lower water-cement ratio) can be used to prepare concrete containing 100 % *thermally treated recycled concrete aggregate* as coarse aggregate. The strength development, although slightly lower than that of the reference concrete indicates that there is an improvement in the quality of the treated recycled concrete aggregate.

4 SUMMARY OF CONCLUSIONS

A preliminary laboratory study was carried out to assess the effectiveness of the thermal treatment methods and to determine the improvement in the quality of the resulting aggregate.

The effectiveness of the thermal treatment methods was assessed by means of optical microscopy and the improvement in the quality of the resulting aggregate was examined by means of concrete technological and strength tests on mortar and concrete mixes. On the basis of the results obtained, the following conclusions may be drawn:

- Stepwise treatment of recycled concrete aggregate, for relatively short duration periods from room temperature up to a temperature of 800 °C produced the same effects as a one-step treatment from room temperature to 800 °C regardless of the aggregate fraction used. Both methods of treatment hardly affected the integrity of the aggregate particles and resulted also in excellent separation of the cement paste or mortar from the aggregate particles. These two treatment methods were classified as the most effective methods of all the treatment methods used.
- Stepwise thermal treatment of recycled concrete aggregate, with each step a relatively longer period from room temperature up to a temperature of 800 °C also yielded reasonably good results. The effectiveness of this treatment method was classified as good.
- Stepwise thermal treatment of recycled concrete aggregate, for a relatively short duration period from room temperature up to a temperature of 650 °C produced reasonably good results with regard to preservation of the integrity of the aggregate particles, regardless of the aggregate fraction used. The method was, however, found not to be very effective in separating the cement paste or mortar from the aggregate particles. On the basis of this, the method of treatment was classified as moderately good.
- The results of technological and strength tests, performed on concrete specimens using a sample of thermally treated concrete aggregate (one-step treatment of the recycled aggregate from room temperature to 800 °C) as coarse aggregate showed reasonably good results compared to conventionally used river gravel.

Although this study is a preliminary one, the results suggest that thermal treatment of recycled concrete aggregate at a temperature of about 800 °C can yield good quality aggregates, with properties which are reasonably comparable to conventionally used river gravel and –sand aggregates.

One remarkable aspect of the study is that although heating of the recycled concrete aggregate at a temperature of 650 °C somehow preserved the integrity of the aggregate particles, it could not effectively separate the cement paste or mortar from the aggregate particles. If this treatment method is combined with mechanical separation, for example by means of mechanical shaking or vibration, the extent of separation of the cement paste and mortar from the aggregate particles may considerably be improved. It is therefore recommended to investigate thermal treatment processes at similar or lower temperatures in combination with mechanical vibration or shaking. This combined thermal-mechanical treatment process may increase the effectiveness or optimise the separation of the cement paste or mortar from the aggregate particles.

It would also be worthwhile to investigate the influence of the particle size of the crushed concrete (or demolished concrete rubble) on the treatment process.

Furthermore, it would be beneficial for the economy of the process to find applications for the fine fraction of the treated recycled concrete for example for use as a binder in the field of building and construction.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Evaluation of solid-stabilized products made from Cr(VI)-containing ferrochrome bag-filter dust

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South Africa produces 43% of the world's ferrochrome. The greatest risk to health and the environment resulting from these operations lies in the toxic, carcinogenic Cr(VI)-containing bag-filter dust (BFD) and sludge obtained from the gas cleaning systems. It is estimated that 100 kt of BFD and sludge are produced per annum. Water leaching tests of BFD indicate that, apart from Cr(VI), the alkaline leachate contains Na, K, SO_4 and Cl. The immobilization of Cr(VI) and salts in cement blocks and fired clay bricks was investigated in this study.

Cement blocks were prepared by mixing crushed slag from ferrochrome and electric arc furnaces with Portland cement (9%) and BFD (15%). These blocks were then cured for 56 days. Water leaching tests conducted on crushed cured blocks indicated that 98% of the Cr(VI) and 50% of the salts added via BFD were immobilized. Compression strengths exceeding 11 Mpa were measured for these cement blocks. The addition of $FeCl_2$ (1.25%) improved the Cr(VI) immobilization. Partial immersion of whole blocks in water indicated that nearly all the Cr(VI) and 98% of salt originating from the BFD were retained.

Fired clay bricks containing up to 50% BFD were prepared. A firing temperature of 1200 °C for 6 hours was required to immobilize Cr(VI) and salts in excess of 99.5% and 93.6%, respectively, as judged by water leaching tests on the crushed material.

The crushed materials from fired clay bricks and cement blocks were subjected to Acid Rain and the US EPA TCLP leaching procedures. The concentrations of Ba, Pb, V, Cr, and Mn were measured in the leachates and their potential impact on the environment assessed according to the Guidelines issued by the South African Department of Water Affairs and Forestry. Leaching of these toxic elements was lower from the crushed, fired clay bricks than from the crushed, cured cement blocks, indicating that clay bricks are the preferred form of stabilization of the ferrochrome BFD.

1. INTRODUCTION AND OBJECTIVES

The South African ferrochrome industry supplies nearly half of the world's requirement of Cr in the form of chromite ore and ferrochromium (FeCr) metal which are used mainly in the manufacture of stainless steel, chromium metal and chemicals. Ferrochromium metal is produced in submerged arc, open-top or closed furnaces where chromite ore, coal, char, silica and limestone are added. The products are ferrochromium metal, slag and a chromate-containing bag-filter dust (BFD) or sludge. The latter poses the greatest risk to health and the environment as chromate or Cr(VI) is toxic, carcinogenic and highly soluble [1]. There are currently 10 ferrochrome producers in South Africa and for 1998 it was estimated that this industry produced 2.7 Mt ferrochrome metal, slag and 100 kt Cr(VI) containing BFD and sludge [2].

In order to minimize the immediate impact on the environment, BFD is added to water, treated with ferrous sulphate or chloride, and pumped to sealed and lined dams for temporary storage. This treatment chemically reduces the immediately soluble hexavalent chromium released from BFD to the less toxic trivalent form as an insoluble $Cr_xFe_{1-x}(OH)_3$ precipitate [3]. At the same time it increases the salt load of this system, which is of concern in a semi-arid country such as South Africa.

Unfortunately, this treatment is only a temporary solution as the treated BFD continues to leach Cr(VI) though to a lesser extent. A long-term treatment option is required to minimize the impact of BFD and sludge on the environment and natural water resources. The work reported in this paper deals with the manufacture of solid-stabilized products (cured cement blocks and fired clay bricks) using BFD and other wastes generated in the local ferro-alloys industry in order to immobilize the Cr(VI) and salts contained in these wastes. The degree of stabilization and the potential toxicity of these products were evaluated by leaching tests in compliance with stipulated Guidelines [4] set by the South African Department of Water Affairs and Forestry (DWAF).

2. CHARACTERIZATION OF WASTES

Crushed (< 10 mm) ferrochrome slag, BFD, brine (recycle water obtained from BFD treatment plant) were obtained from a ferrochrome producer in the North West Province. Clay was obtained from a brick manufacturer in the vicinity. Ordinary Portland Cement (OPC) was obtained from a local producer. A crushed (< 10 mm) electric arc furnace (EAF) slag containing wuestite (FeO) was also used in cement mixes to promote the immobilization and reduction of chromate in these systems. The chemical analyses of the major components in these solids are shown in Table 1, together with the amounts of Cr(VI) and salts that were extracted by extensive water leaching tests. Cr(VI) is leached only from BFD, but salts are leached from all waste components, mostly from BFD. The brine obtained from the BFD treatment plant contained: 0.4 g/l Ca, 1.6 g/l K, 3.8 g/l Na, 5.9 g/l Cl, 7.1 g/l SO_4 and a Total Dissolved Solids (TDS) content of 20.5 g/l.

3. PRODUCTION OF CEMENT BLOCKS

The recipes used in the preparation of 14 different batches of cement mixes are shown in Table 2. In all the mixes, 620g of OPC was used with different proportions of BFD, FeCr and EAF slag. The total mass of solids in each mix was 7 kg. The amounts of $FeCl_2$, water and brine used to prepare the mixes are also shown. The various batches were mixed manually, poured into plastic bottles and allowed to cure at room temperature. This formed cylindrical blocks 90 mm in diameter and of equal height, with an average volume of 570 ml and 1.3 kg dry cured mass. Some of the mixes were cast into standard building brick molds for compression strength tests. After curing for 56 days the blocks were dried for 2 hours at 120 °C to stop the curing process and then crushed to < 10 mm and subjected to leaching tests.

Table 1. Chemical analyses of solids (major components, > 0.1%)

	Composition, %				
Component	FeCr slag	EAF slag	BFD	OPC	Clay
Na_2O	<2.7	<2.7	<2.7	128 ppm	0.43
MgO	7.5	3.3	23.2	2.48	1.47
Al_2O_3	12.7	3.4	4.5	4.47	13.4
SiO_2	53.5	15.4	47.1	21.2	64.7
P_2O_5	<0.1	0.9	<0.1	n.d.	n.d.
SO_4	0.2	0.5	5.7	n.d.	n.d.
K_2O	0.2	<0.1	1.2	0.15	1.42
CaO	2.1	43.4	0.5	60.4	0.71
TiO_2	0.7	0.5	0.2	n.d.	n.d.
Cr_2O_3	12.6	0.3	8.0	<0.2	<0.2
Mn_2O_3	0.3	4.3	0.5	0.27	0.15
Fe_2O_3	9.4	27.2	4.3	2.61	8.05
Cl	<0.1	<0.1	1.0	n.d.	n.d.
ZnO	<0.1	<0.1	1.7	n.d.	n.d.
Ga	<0.1	<0.1	0.1	n.d.	n.d.
Total	99.2	99.2	98.0	91.6	90.3
Cr(VI), g/kg	0	0	1.22	0	0
TDS, g/kg	6.65	34.55	92.55	4.70	0

n.d. = Not determined

Table 2. Composition of cement mixes

Mix	Mass, g						
No	Cement	FeCr	BFD	EAF	$FeCl_2$	Brine	Water
A	620	6170		210			1050
C	620	5960	210	210	8	1050	
D	620	5960	210	210	8		1050
H	620	5540	210	630			1050
J	620	5960	420			1050	
K	620	5540	420	420	16	1050	
M	620	5540	420	420		1050	
N	620	5540	420	420			1050
O	620	5120	420	840			1050
P	620	4700	420	1260			1050
S	620	5039	630	630	81		1050
U	620	3790	840	1680	70		1050
W	620	3142	1050	2100	88		1050
X	620	2512	1050	2730	88		1050

4. EVALUATION OF CURED CEMENT BLOCKS

The compressive strengths of standard size (223 X 108 X 76 cm^3) cement blocks cured for 56 days were measured with a Tinius Olsen Press. The compression strengths of 18.4, 18.2 and 11.7 Mpa were measured for blocks N, O and P, respectively. Extensive studies regarding the compressive strength of cement bricks made from ferrochrome BFD, slag and various types of cement have been reported on by Smit, *et al.* [5]. The compressive strengths, obtained in the current study, were of the same order of magnitude as those found for similar materials by Smit, *et al.* [5] in the previous study. That study indicated that most of the bricks obtained the required compressive strength of 7 Mpa after 14 days curing and complied with the standards set by the South African Bureau of Standards [6]. The current investigation, therefore, focussed more extensively on the immobilization of Cr(VI) and salts in these systems, as there is sufficient evidence that the required compressive strength can be achieved without any difficulty. Smaller cement blocks, using less material, were prepared for this purpose.

The cured, crushed cement blocks were subjected to a water-leaching test based on the German DIN 38414 procedure [7]. This involved agitating 100 g of crushed solid in 1000 ml of water placed in a closed container on a horizontal laboratory shaker for 24 and 48 hours and measuring the Cr(VI) and salt concentrations in the filtered leachate. The Cr(VI) concentration was determined by spectrophotometry according to the procedure described by Bartlett [8] using a Hewlett Packard 8452 Diode Array spectrometer. The TDS or salt concentrations were determined by gravimetry after evaporating a known volume of leachate to dryness in a porcelain dish on a hotplate. The masses of Cr(VI) and salt leached from the crushed, cured cement blocks, expressed in mg/kg, were compared to those originally added to the mix (Tables 1 and 2 above). On this basis the percentage stabilization of Cr(VI) and TDS in cured cement blocks was calculated. These results are shown in Table 3.

Table 3. Cr(VI) and salt stabilization in cement blocks cured for 56 days

Mix	Cr(VI), mg/kg			TDS, g/kg		
No	Added	Leached	% Stab.	Added	Leached	% Stab.
A	0.00	0.0	0.0	11.06	13.57	-22.7
C	36.55	1.64	95.5	17.82	11.83	33.6
D	36.55	1.15	96.9	14.75	10.68	27.6
H	36.55	4.94	86.5	15.31	11.37	25.7
J	73.09	15.73	78.5	18.45	10.65	42.3
K	73.09	2.11	97.1	22.35	10.98	50.9
M	73.09	5.07	93.1	20.12	12.94	35.7
N	73.09	4.38	94.0	17.05	7.95	53.3
O	73.09	4.80	93.4	18.73	12.52	33.1
P	73.09	3.07	95.8	20.40	12.44	39.0
S	109.64	4.48	95.9	31.96	14.88	53.4
U	146.18	0.42	99.7	37.16	18.37	50.6
W	182.73	10.27	94.4	43.97	19.94	54.7
X	182.73	3.50	98.1	46.48	21.04	54.7

The poorest Cr(VI) stabilization (78.5%) was found for blocks made from mix J, where no EAF slag or $FeCl_2$ was added. On the other hand, where only crushed EAF slag was added to the mix, i.e., mixes M, N, O, P but in increasing amounts, the Cr(VI) stabilization improved from 93.1 to 95.8 per cent. Generally the highest Cr(VI) stabilizations were observed where both EAF slag and $FeCl_2$ were added (mixes C, D, K, S, U, W, and X). It should be noted that, when more BFD was added to the mix, increasing the Cr(VI) content from 36.55 to 182.73 mg/kg, the same, effective immobilization of Cr(VI) was achieved by increasing the addition of $FeCl_2$ and EAF slag. The results shown in Table 3 indicated that lower salt stabilizations (30 to 55 per cent) were observed for crushed cement blocks and that these also improved with increasing salt added to the mix.

The stabilization of Cr(VI) and TDS in whole cement blocks was also investigated by partially immersing blocks in 1 liter of water without agitation for 21 days. The water was replaced with fresh water every 7 days. The leachates were analyzed for Cr(VI) and TDS concentration and the amount leached from the blocks compared to those originally added to the mix to calculate the percentage stabilization. The results of this study are shown in Table 4. The Cr(VI) and salt stabilization values for whole cement blocks are significantly higher than the corresponding data (Table 3) for crushed cement blocks. The observed improvement, particularly in salt stabilization for whole blocks, is attributable to slower diffusion of salts from the larger blocks than the smaller (< 10 mm) crushed material. Hence it may be concluded that whole cement blocks will effectively retain all the undesirable components in BFD.

The mechanism of Cr(VI) immobilization in these cured cement blocks was elucidated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). No Cr(VI)-containing mineral phase could be identified in the cured cement blocks (mixes C, and L). However, SEM studies did indicate that a Ca-Mg-Al-silicate phase incorporates the Fe-Cr hydroxide formed as a result of the interaction between BFD, $FeCl_2$ and EAF slag. This mechanism agrees with those suggested by Omotoso, *et al.* [9] for similar systems. Fe-Cr hydroxide in these systems would more than likely have taken place during the initial preparation of the mix prior to onset of the cementitious reactions expected to occur during the curing of cement blocks. It is also suggested that any Cr(VI) released after the initial mixing could have been reduced by the mineral wuestite contained in EAF slag by a chromate adsorption-reduction mechanism as has been observed for magnetite [10].

Table 4. Cr(VI) and salt stabilization in whole cement blocks.

Mix	Cr(VI), mg/kg			TDS, g/kg		
Type	Added	Leached	% Stab.	Added	Leached	% Stab.
A	0	0	0	11.06	0.15	98.6
C	36.55	0	100.0	17.82	0.26	98.0
H	36.55	0.01	100.0	15.31	0.19	98.7
K	73.09	0.03	100.0	22.35	0.35	98.4
P	73.09	0.11	99.9	20.40	0.23	98.9
S	109.64	0.02	100.0	31.96	0.35	98.9
U	146.18	0.03	100.0	37.16	0.71	98.1
W	182.73	0.03	100.0	43.97	0.74	98.3
X	182.73	0.02	100.0	46.48	0.63	98.6

5. PRODUCTION OF FIRED CLAY BRICKS

Different masses of clay, BFD and salt were mixed in a mechanical mixer with a minimum amount of water (20 per cent of the total solids mass). The compositions of 8 different batches are shown in Table 5. The mixes were then pressed into compact bricks with dimensions 42mm X 78mm X 115mm using a Tinius Olsen Press at 25 kN. The bricks were allowed to dry at room temperature for a week before firing in a kiln. The kiln temperature was increased from 25 to 1200 °C over 48 hours, kept constant for 6 hours and then allowed to cool to room temperature over 48 hours.

Table 5. Composition of mixes used in the manufacture of fired clay bricks

Mix	Mass, g					
Number	Clay	BFD	$K_2Cr_2O_7$	NaCl	Na_2SO_4	Dry Brick
1	400	400	0	0	0	800
2	400	400	1	0	0	801
3	400	400	2	0	0	802
4	400	400	4	0	0	804
5	400	400	0	10	10	820
6	400	400	0	20	20	840
7	400	400	0	40	40	880
8	800	0	0	40	40	880

Table 6. Stabilization of Cr(VI) and salt in crushed clay bricks fired at 1200 °C

Mix	Cr(VI), mg/kg			TDS, g/kg		
No	Added	Leached	% Stab.	Added	Leached	% Stab.
1	609	0.58	99.9	46.275	1.675	96.4
2	1050	2.19	99.8	47.466	1.375	97.1
3	1489	1.52	99.9	48.653	1.300	97.3
4	2365	2.42	99.9	51.020	1.275	97.5
5	594	3.15	99.5	69.537	1.000	98.6
6	580	2.48	99.6	91.690	4.650	94.9
7	554	1.17	99.8	132.977	5.300	96.0
8	0.0	0.07	0	90.909	5.850	93.6

The fired clay bricks were crushed to < 10 mm and leached with water using the same method as for the cured, crushed cement blocks. Similarly, Cr(VI) and TDS concentrations were measured in the filtered leachates and the amounts of these components leached from crushed, fired clay bricks were calculated. These results are shown in Table 6 and compared to the amounts originally added to the clay bricks. From these data the percentage Cr(VI) and TDS stabilized in these systems were calculated.

Higher Cr(VI) and TDS stabilization values were observed for crushed fired clay bricks than for the cured cement blocks (Table 3). This result is even more significant since more Cr(VI) and TDS were added to the clay bricks than to the cement blocks. For instance, the maximum amount of Cr(VI) added (50 per cent BFD and $K_2Cr_2O_7$) to a clay brick was 2365 mg/kg (mix 4, Table 6) whilst for a cement block the corresponding value was only 183 mg/kg (15 per cent BFD, mixes W and X, Table 3). Similarly TDS additions in the case of clay bricks (mix 7, Table 6) 133 g/kg TDS was added with 96 per cent stabilization whereas for a cement block (mix X, Table 4) 46.5 g/kg TDS was added with only 55 per cent stabilization. Therefore it can be concluded that both Cr(VI) and TDS stabilization was more effective in crushed, fired clay bricks than in crushed, cured cement blocks.

The mineralogy of fired clay bricks (mix 4, Table 5) was investigated with a JEOL 733 Superprobe to identify phases that were responsible for the effective Cr(VI) and salt stabilization in these systems. Chromium was found in spinel and glass phases that were also found in BFD. In addition, a major amorphous Mg-Al-Fe-Si phase consisting of Cr_2O_3 (0.8 to 2.1%), MnO (0.2 to 0.5%), ZnO (3.6 to 5.0%), Na_2O (6.2 to 7.8%), SO_3 (up to 2.1%) and K_2O (1.7 to 2.8%) was identified. The presence of sulphur in this amorphous phase could be an indication that chromate, accompanied by its reduction product and salts were incorporated into it. It is believed that this amorphous Mg-Al-Fe-Si phase is responsible for the Cr(VI) and TDS stabilization in the fired clay bricks.

6. POTENTIAL TOXICITY OF SOLID-STABILIZED PRODUCTS

The success of the exercise to produce solid-stabilized products with chromate- containing BFD is ultimately judged by the extent to which these products can safely be disposed of without posing a threat to health and the environment. For this purpose, the results of the leaching tests were evaluated in terms of the recently published DWAF [4] Guidelines. According to these Guidelines, the acceptability of disposal of hazardous wastes is based on the relationship between the acute ecotoxicity of a substance, expressed as LC_{50} (mg/l), and the Estimated Environmental Concentration (EEC) expressed in ppb. LC_{50}, the median lethal dose, is a statistical estimate of the amount of chemical which will kill 50 per cent of a given population of aquatic organisms under standard conditions. EEC represents an assessment of the exposure of a hazardous substance in the treated waste should it enter into the environment. EEC is measured in ppb and is calculated as 0.66 x the dose (g/ha/month). For Cr(VI) the DWAF Guidelines use a LC_{50} value of 0.2 mg/l.

In order to conduct this exercise for the solid-stabilized products it was assumed that each of the 10 local ferrochrome producers produce an equal amount of the total 100 ktpa Cr(VI)-containing waste and each has a 30 ha dumping site available to dispose of the solid-stabilized products. Assuming 10 and 50% BFD to be incorporated in cement blocks and fired clay bricks, respectively, the rate of dumping of these products would amount to 2.684×10^5 and 5.368×10^4 kg/ha/month. Based on this information and the results of the above Cr(VI) water leaching tests for a number of whole and crushed cement blocks and clay bricks the EEC values were calculated (Table 7). The DWAF guidelines recommend that an EEC value of a tenth of the LC_{50} would pose no threat to the environment. Hence an EEC Cr(VI) value of 20 ppb or less would be acceptable. Only whole cement blocks H, K, U and X together with crushed brick 1 comply with this requirement. For all the other products tested, the Cr(VI) leaching would imply that these products still pose a threat to the environment.

Table 7. Chromate toxicity of solid-stabilized products

Mix No	Curing Time Days	Block type	Leaching Time Days	Mass kg	Cr(VI) Conc mg/l	Volume ml	Cr(VI) leached mg/kg	EEC ppb Cr(VI)
H	56	whole	7	1.366	0.024	730	0.0128	2.27
K	56	whole	7	1.360	0.064	720	0.0339	6.00
U	56	whole	7	1.315	0.038	540	0.0156	2.76
X	56	whole	7	1.247	0.011	630	0.0056	0.99
K	56	crushed	1	0.100	0.159	1000	1.5900	281.7
K	120	crushed	1	0.100	0.069	1000	0.6900	122.2
U	56	crushed	1	0.100	0.028	1000	0.2800	49.6
X	56	crushed	1	0.100	0.20	1000	2.0000	354.3
1		crushed	1	0.100	0.031	1000	0.31	11
5		crushed	1	0.100	0.235	1000	2.35	83
7		crushed	1	0.100	0.117	1000	1.17	41

The leaching of other potentially toxic components from solid-stabilized products was evaluated by Acid Rain and the TCLP tests prescribed by the US EPA [11]. For the Acid Rain test, 100 g of crushed solid was contacted with 2000 ml water carbonated to a pH value of 3.95 in a sealed glass vessel agitated head-over-heels at 30 r/min for 24 hours. Concentrations of 10 elements in the filtered leachates of both tests were measured by ICP mass spectrometry in the Analytical Science Division of Mintek. The Acid Rain test results are shown in Table 8, and the corresponding data for the TCLP test are shown in Table 9. In both Tables, the concentrations of components that were above the detection limits are highlighted.

Table 8. Acid Rain test results on crushed solid-stabilized products

Mix	Final	Concentration, mg/l									
No	PH	V	Cr	Mn	As	Se	Ag	Cd	Ba	Hg	Pb
A	6.33	<0.1	<0.1	<0.1	<0.5	<1.0	<0.1	<0.05	<0.05	<0.05	<0.05
C	5.82	<0.1	<0.1	<0.1	<0.5	<1.0	<0.1	<0.05	<0.05	<0.05	**0.08**
H	6.19	<0.1	**0.12**	<0.1	<0.5	<1.0	<0.1	<0.05	<0.05	<0.05	<0.05
K	5.84	<0.1	**0.12**	<0.1	<0.5	<1.0	<0.1	<0.05	<0.05	<0.05	<0.05
N	6.02	<0.1	**0.21**	<0.1	<0.1	<1.0	<0.1	<0.1	<0.05	<0.1	<0.05
P	5.94	<0.1	**0.14**	<0.1	<0.1	<1.0	<0.1	<0.1	<0.05	<0.1	<0.05
1	n.d.	<0.1	<0.01	**0.016**	**0.005**	<0.02	<0.04	<0.01	**0.011**	<0.02	<0.02
4	n.d.	**0.123**	**0.039**	**0.023**	<0.01	<0.02	<0.04	<0.01	**0.013**	<0.02	<0.02
7	n.d.	**0.012**	**0.043**	**0.019**	<0.01	<0.02	<0.04	<0.01	**0.019**	<0.02	<0.02
8	n.d.	<0.01	<0.01	**0.535**	<0.01	<0.02	<0.04	<0.01	**0.017**	<0.02	<0.02

n.d. Not determined

For the Acid Rain test, V, Cr, Mn and Ba concentrations were detected in the leachates of a number of solid-stabilized products. Higher Cr concentrations were observed in tests on cured cement blocks than in the corresponding water leaching tests. This is presumably due to a lower pH of leaching and the contribution of Cr(III) to the total Cr concentration measured by the ICP method. The concentrations of V, Mn and Ba observed in the Acid Rain leaching tests on fired clay bricks may have originated from the clay. (The concentrations of As measured for crushed fired clay brick mix 1 and Pb for crushed cured cement block C were regarded as exceptions, and are ascribed to contamination and not considered to be significant). The potential impact on the environment of the leachable elements was assessed according to the DWAF Guidelines. The corresponding calculated EEC values are shown in Table 10.

Table 9. TCLP test results on crushed solid-stabilized products

Mix No	Final pH	V	Cr	Mn	As	Se	Ag	Cd	Ba	Hg	Pb
		Concentration, mg/l									
A	11.12	<0.1	<0.1	<0.1	<0.5	<1.0	0.67	<0.05	**0.26**	<0.05	<0.05
C	10.39	<0.1	<0.1	<0.1	<0.5	<1.0	<0.1	<0.05	**0.23**	<0.05	**0.34**
H	11.00	<0.1	0.26	<0.1	<0.5	<1.0	<0.1	<0.05	**0.24**	<0.05	**0.15**
K	10.43	<0.1	<0.1	<0.1	<0.5	<1.0	<0.1	<0.05	**0.23**	<0.05	<0.05
N	6.42	<0.1	<0.1	**16.5**	<0.1	<1.0	<0.1	<0.1	**0.88**	<0.1	<0.05
P	7.17	<0.1	<0.1	**23**	<0.1	<1.0	<0.1	<0.1	**0.86**	<0.1	**0.71**
1	n.d.	<0.05	<0.1	**0.13**	<0.03	<1	<0.05	<0.02	**0.11**	<0.01	**0.14**
4	n.d.	<0.05	**0.14**	**1.7**	<0.03	<1	<0.05	<0.02	**0.25**	<0.01	<0.05
7	n.d.	<0.05	**0.17**	**0.11**	<0.03	<1	<0.05	<0.02	**0.13**	<0.01	<0.05
8	n.d.	<0.05	<0.1	**0.99**	<0.03	<1	<0.05	<0.02	**0.13**	<0.01	<0.05

n.d. Not determined

Table 10. Toxicity evaluation of crushed, solid-stabilized products

Element	Mix No	Leaching Time Hours	Leaching medium	Mass kg	Conc mg/l	Vol ml	Amount leached mg/kg	EEC ppb
Cr	K	20	Acid Rain	0.100	0.12	2000	2.4	425
	7	19	TCLP	0.100	0.17	2000	3.4	120
	4	20	Acid Rain	0.100	0.039	2000	0.78	28
Mn	N	19	TCLP	0.100	16.5	2000	330	58458
	4	20	Acid Rain	0.100	0.023	2000	0.46	16
	7	19	TCLP	0.100	0.11	2000	2.20	78
Pb	8	20	Acid Rain	0.100	0.535	2000	10.7	379
	P	19	TCLP	0.100	0.71	2000	14.2	2515
	1	19	TCLP	0.100	0.14	2000	2.8	99
V	4	20	Acid Rain	0.100	0.123	2000	2.46	87
Ba	N	19	TCLP	0.100	0.88	2000	17.6	3117
	4	19	TCLP	0.100	0.25	2000	5.0	177

The TCLP leaching tests indicate that the elements Cr, Mn, Ba and Pb were mobilized from both cement blocks and clay bricks. The results shown in Table 9 suggest that generally lower concentrations of these elements were mobilized from fired clay bricks than from cured cement blocks.

According to the DWAF Guidelines, the calculated EEC values for stabilized waste should be less than a tenth of the LC_{50}. For Cr, Mn, Pb, V and Ba, maximum EEC values of 20, 300, 100, 1300 and 7800 ppb, respectively, are stipulated. Based on these values, the results shown in Table 10 indicate that immobilization of Ba and V in crushed stabilized solids is satisfactory. However, Pb and Cr in all these products pose a threat to the environment and in some of the samples the immobilization of Mn is insufficient. The results in Table 10 indicate that the crushed fired clay bricks yield lower calculated EEC values than the cured cement blocks.

Preliminary estimates have indicated that production costs for the manufacture of fired clay bricks amount to R190 per ton of BFD treated in the manner described in this study. The corresponding cost for the stabilization of BFD in cured cement blocks amount to R235 per ton. The production of fired clay bricks is therefore the most cost-effective treatment option.

In this regard, it should also be noted that local ferrochrome producers have started to recycle BFD rather than to dump the material. This is achieved by mixing fine chromite ore with BFD in the form of sintered briquettes that are then fed to the ferrochrome furnaces.

7. CONCLUSIONS

This study has indicated that soluble Cr(VI) and salt contained in BFD generated in the South African ferrochrome industry can be immobilized in cured cement blocks and fired clay bricks. The latter option is more effective. Water, Acid Rain and TCLP leaching tests conducted on crushed samples of both solid-stabilized products have indicated that more than the permitted (according to DWAF Guidelines) amount of Cr(VI) leached from these solids. Only water leaching tests on whole cured cement blocks have indicated that less Cr(VI) than the permitted values are released and can therefore be disposed of in this manner without posing a threat to the environment.

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Waste Materials in Construction
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Durability study of a sewage sludge-cement-sand system and its environmental impact

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One of the main objectives of the work is to present an effective alternative for the final destination of urban wastewater sewage sludge, by means of its inclusion in mortar or concrete. To this end, a durability study was performed on the system. The study consisted in subjecting the mortar samples to a process of accelerated carbonation and subsequently assessing the products of the carbonation by ^{29}Si RNM-MA nuclear magnetic resonance of solids and its environmental impact by the NEN-7345 monolithic leaching test. Carbonation at very high concentrations of CO_2 favours the polymerization of the C-S-H and the breakdown of the ettringite, which affects the leaching processes and the concentration of heavy metals and other pollutants in the leachates obtained from the NEN 7345 leaching test.

1. INTRODUCTION

The study consists in including wastewater sewage sludge in a building material bound with Portland cement. Wastewater sewage sludge is a waste product with toxic potential, and it is therefore necessary to make an environmental assessment of the material after subjecting it to a durability test such as carbonation.

Assessment of the environmental quality of the final product and the consequent guarantee of its use in the building industry demand that it meets a number of requisites, one of which is that the effluents extracted by water action should be contamination-free, or at least that the concentration of contaminants should be below certain pre-set limits. For this purpose a number of leaching tests must be carried out, such as the Netherlands Tank Leaching Test (NTLT) [1].

1.1. Characterisation of the sludge

The sewage sludge used is a biological sludge from the waste waters generated in the surroundings of Manresa, close to the city of Barcelona. The sludge was treated by the classic process of anaerobic digestion. In general, the pH was fairly constant, with a moderately basic value between 7 and 8.

Part of the chemical characterisation corresponds to the determination of the total heavy metals and heavy metals extractable.

- *Total heavy metal content of the sludge:* Determining this is of fundamental importance since it enables us to compare and establish the degree of suitability of the materials produced according to the leaching test and thereby ascertain what proportion of the total has been extracted. The solutions obtained are analysed by plasma source atomic emission spectrometry (ICP). The results obtained for the sludge from the waste water treatment plant are set out in *Table 1.*

Table 1
Heavy metal content of the Manresa Treatment Plant sludge, by total sample digestion. The results are expressed in mg of metal per kg sample of dry waste analysed

Cd	Cu	Mn	Ni	Pb	Cr	Zn	Ba
<0.58±0.05	157.43±14	391.65±2.7	60.61±5.75	116.18±3.0	202.11±6.4	4130±353	618.8±72.2

- *Heavy metals extractable in the sewage sludge in an acid medium.* The standard used was ISO/CD 11466 [2]. They were also analysed by plasma source atomic emission spectrometry (ICP). The results are shown in *Table 2.*

Table 2
Concentration of heavy metals extractable in sewage sludge by acid digestion according to ISO/CD 11466 standard. The results are expressed in mg of metal per kg sample of dry waste analysed

Cd	Cu	Mn	Ni	Pb	Cr	Zn	Ba
<0.6±0	152.27±1,6	331.62±3	46.13±4,5	101.71±3.8	197.05±2.2	3931±21.4	373.67±7.2

The remaining toxic contaminants: sulphates, chlorides, phosphates and total organic carbon (TOC) were determined according to the leaching test for German standard DIN 38414 S4 [3], see *Table 3.*

Table 3
Total organic carbon and sulphate, chloride and phosphate content in the wastewater sewage sludge

Contaminant	*Concentration*	*Analysis Technique*
TOC (mg C / l)	807.8±0,0	TOC analyser
Conductivity (μS/cm)	1611	Conductometer
Chlorides (mg/l)	94.47±0,0	Ionic chromatography
Phosphates (mg/l	35.40±0.001	Ionic chromatography
Sulphates (mg/l)	384.01±0.0	Ionic chromatography

1.2. The sludge mortar mixes

The mortar was composed of: wet sludge, calcareous sand, Portland I 45/A cement and tap water, the quantity of which was determined with the flow table test [4]. The conditions of mortars processing are according to standard UNE 80-101 [5]. In some of the mortar mixes, calcium chloride was added as an accelerator and Escucha fly ash was used as a partial cement replacement. The calcium chloride was added with the aim of improving the cement's hydration to counteract the effects of the organic material contained in the sludge.

The sludge mortar mixes complied with the results of another study on physical stabilisation/solidification in cement pastes containing sludge, in which 35% to 25% wet sludge in the mixture was found to be the maximal amount compatible with strength requirements. The mixes studied are set out in *Tables 4* and *5*.

Table 4
Nomenclature and mixes of mortars containing wet sludge from the Manresa Treatment Plant, without added fly ash

	Sludge/binder	Water(g)*	Sludge(g)	Cement (g)	Sand (g)	Additive
(1) CM25A	1:1	62	450	450	900	
(2) CM25A+ad	1:1	62	450	450	900	$CaCl_2$
(3) CM25B	1:1	72	500	500	1000	
(4) CM25B+ad	1:1	72	500	500	1000	$CaCl_2$
(5) CM35A	1.4:1	65	630	450	720	
(6) CM35A+ad	1.4:1	65	630	450	720	$CaCl_2$
(7) CM35B	1:1	34	700	700	600	
(8) CM35B+ad	1:1	34	700	700	600	$CaCl_2$

Table 5
Nomenclature and mixes of mortars containing wet sludge from the Manresa Treatment Plant, with added fly ash

	Sludge/binder	Water(g)*	Sludge(g)	Cement (g)	Sand (g)	fly ash
(9) CM25L5CV	1:1	90	500	475	1000	25
(10) CM25L10CV	1:1	90	500	450	1000	50
(11) CM25L15CV	1:1	90	500	425	1000	75
(12) CM25L25CV	1:1	90	500	375	1000	125
(13) CM35L5CV	1:1	90	700	665	600	35
(14) CM35L10CV	1:1	90	700	630	600	70
(15) CM35L15CV	1:1	90	700	595	600	105
(16) CM35L25CV	1:1	90	700	525	600	175

* The amount of water is the water added to the mix without counting the water contained in the sludge. The sludge humidity was 68%.

2. DURABILITY: ACCELERATED CARBONATION

After a 60-day curing process in a damp chamber, the test specimens in different dosages were dried to a relative humidity of 63 ± 2%. At this humidity the depth of the initial carbonation front was determined with a 1 % phenolphthalein solution in 70% ethanol. Later on, five faces of the test specimens were impermeabilised to get a one-directional carbonation. The application of the indicator and the measurements of the carbonation front were made following the recommendations in RILEM CPC-18 [6].

The test consisted of an accelerated carbonation based on the process by Ho and Lewis 1983 [7]. It consists of eight cycles of 192 hours each, in a climatic chamber at a temperature of 20°C, a relative humidity of 65% and a 1 atmosphere pressure of 99.99% pure CO_2. The CO_2 injections were up to saturation point.

After undergoing the eight cycles the mortars displayed large carbonation fronts, between 54 and 100%, since these mortars are characterised by their high porosity.

2.1. Products of carbonation

The carbonation products were studied by ^{29}Si RNM-MAS nuclear magnetic resonance of solids. This technique allows the hydration of calcium silicates and the polymerisation of the silicate to be examined, giving an idea of the number of silicon atoms bonded to the basic unit, the silicon tetrahedron. The increase in the number of silicon atoms bonded increases polymerisation.

The RNM-MAS ^{29}Si spectra indicate the degree of polymerisation of the hydrates in the cement paste, and thus the evolution of the C-S-H. The degree of polymerisation is shown according to the chemical environment or displacement band. If we find Q^0 in the sample spectrum, this indicates the presence of monomeric units corresponding to anhydrous calcium silicates. On the other hand, the Q^1 (-80 ppm) and Q^2 (-85, -90 ppm) bands correspond to the hydration of calcium silicates and the formation of C-S-H. The presence of the Q^3 (-94 ppm) and Q^4 (-101.6 ppm) displacement bands corresponds to the polymerisation of the C-S-H [8], which consists in the formation of silica gel when this is carbonated. *See Expression (1.1)*

$$3\,CaO \cdot 2\,SiO_2 \cdot 2\,H_2O + 3\,CO_2 \rightarrow 2\,SiO_2\,(gel) + 3\,CaCO_3 + 3\,H_2O \qquad (1.1)$$

2.1.1. *Results of carbonation products*

Carbonated samples with and without sludge and uncarbonated samples were examined. The results are shown in *Table 6*. The samples with and without sewage sludge which underwent an accelerated carbonation process only have their displacement band at approximately -94 ppm, band Q^3. On the other hand the uncarbonated samples have band Q^1, see *Table 6* and *Figure 1*.

Table 6
Chemical displacements assigned to each band of each sample tested by RMN-MAS of ^{29}Si

	Q^0 (δ ppm)	Q^1 (δ ppm)	Q^2 (δ ppm)	Q^3 (δ ppm)	Q^4 (δ ppm)
CM25A+ad Carbonated				- 94,6	
CM25B+ad Carbonated				- 94,1	
CM35A+ad Carbonated				- 94,6	
CM35B+ad Carbonated				- 92,8	
I 45/A not Carbonated		- 79,0			
I 45/A Carbonated				- 94,6	
CM25L25CV Carbonated				- 94,6	
I 45/A+ fly ash Carbonated				- 94,7	

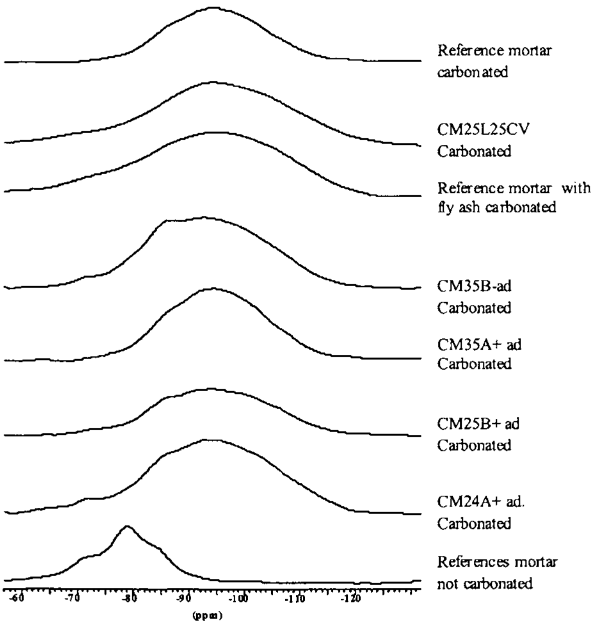

Figure 1. Spectra of ^{29}Si RNM-MAS. There are carbonated samples with sludge, reference carbonated samples without sludge and reference uncarbonated samples without sludge.

2.2. Environmental assessment of carbonated mortars

2.2.1. Results

The carbonation process directly affects the material's properties, and an environmental assessment of this is necessary. This assessment consists in subjecting the mortars to a leaching process after the accelerated carbonation process. The leaching standard used is NEN 7345 [1], which allows the leaching potential to be assessed in matrices that have first undergone a carbonation process with waste stabilised in the long term.

The contaminants studied are:heavy metals (Ba, Cd, Cr, Cu, Zn, Ni, Pb), anions (SO_4^{-2}, PO_4^{-3} and Cl^-) and the soluble total organic carbon (TOC). *Figures 2, 3, 4* and *5* show the results. To value these mortars including sludge after the accelerated carbonation process one must know the contaminant contribution in the leaching by the mortar with Portland cement without sludge, see *Table 7.*

Table 7

Results of the accumulative leaching test (mg/m^2) NEN 7345 for the reference mortar, lime sand Portland I 45/A cement without sewage sludge after the carbonation process.

Contaminants in cement I 45/A (mg/m^2)			
Ba	<0.30±0	Zn	<0.60±0
Ni	<1.5±0	Cu	<0.30±0
Cd	<0.30±0	Cl^-	<88.02±0
Pb	<3±0	SO_4^{2-}	959±3
Cr	<0.60±0		

The results for the accumulative leaching of the reference mortar reveal that the Portland cement does not issue contaminants into the environment, only releasing a small amount of sulphates into the leachate, around 959 mg/m^2 through the carbonation process.

2.2.2. Discussion of leaching carbonated mortars

The concentrations of the toxic contaminants examined in the leaching process with mortars subjected to accelerated carbonation are compared with the results obtained in the mortars which did not undergo an accelerated carbonation process [8].

- Heavy metals: The carbonated mortars displayed accumulated leaching of metals under the *U1* limit of NEN-7345 [1] standard, and showed no kind of environmental restriction for their use. Nevertheless, the levels of copper, nickel and zinc detected are slightly higher in most of the dosages of carbonated mortars than in uncarbonated mortars, *(figures 2* and *3).* In certain dosages there is even a slight presence of manganese. On the other hand, there is a large reduction in barium in carbonated mortars.

Carbonation gives rise to an increase in the concentration of nickel, copper and zinc in the leachates for three reasons: (a) slight increase in the solubility of the metal compounds through the reduction of the pH in the stabilisation system, (b) the decomposing of the ettringite hydrate that had zinc incorporated in its crystalline structure, and (c) the polymerisation of the C-S-H, releasing metal cations which were linked to the Si-O groups [9].

The amount of barium element leaching is much lower in the carbonated system, due to its lower insolubilisation through the formation of $BaCO_3$ and $BaSO_4$, with lower solubilities than the barium hydroxide. The $BaCO_3$ is formed by the carbonation process and the $BaSO_4$ through the decomposition of the ettringite. Carbonation decomposes the ettringite to form calcium carbonate, alumina gel and gypsum [10]. See *Expression (1.2).* The gypsum is soluble, releasing sulphates into the leachate.

- Sulphates, chlorides and phosphates: There is an increase in both chlorides and sulphates in all the dosages of carbonated mortars. The accumulative leaching of chlorides, even at higher concentrations, is under U_1. On the other hand the sulphates, depending on the dosage, are either under the U_1 limit, or between U_1 and U_2, see *Figure 4,* which according to the standard would not involve any environmental restriction for their use, but they would require treatment when their useful life ends. The leaching of sulphates in all the mortars subjected to the accelerated carbonation test is greater than in the non-carbonated mortars, whose leaching was limited to a surface washing. The retention of the sulphates was caused by the formation of ettringite in the hydration of Portland cement. However, in the carbonation process the ettringite undergoes a decomposition process [10], *Expression (1.2)* In this ettringite decomposition process gypsum is formed, which has greater solubility. The ettringite has Kps $\cong 10^{-40}$ at 20 °C and the gypsum Kps $\cong 3.8\ 10^{-5}$.

$$3\ CaO.\ Al_2O_3\ 3\ CaSO_4.\ 32\ H_2O + 3\ CO_2 \rightarrow 3\ CaCO_3 + 3\ \underset{\text{gypsum}}{(CaSO_4.\ 2\ H_2O)} + \underset{\text{alumina gel}}{Al_2O_3\ x\ H_2O} + (26\text{-}X)\ H_2O \quad (1.2)$$

Phosphates are also not detected in the leachates of the carbonated mortars, as occurred with the non-carbonated mortars.

A higher concentration of chlorides in the eluates of the leaching process through the decomposition of Friedel's salt, formed in the hydration process of the cement paste of the mortar [11], see *Figure 4.*

-Total soluble organic carbon (TOC): In the accumulative leaching of all the carbonated dosages there was a large reduction in the TOC concentration, and thus a greater retention power of the matrices formed after the carbonation process.

In carbonated mortars there is an increase in the sinuousness of the porous system, and therefore a decrease in porosity. The system's sinuousness makes the leaching process more difficult. This effect is positive on the organic leachates, which are less affected by the polymerisation of the C-S-H, the reduction in the pH of the mortar system and the decomposition of the ettringite in which $CaCO_3$ and gypsum are formed. The amount of leached organic carbon (TOC) is consequently less in all the cases, (*figure 5*).

- The leaching liquids obtained from these carbonated mortars display a reduction in the pH from 12 to 8. The pH value of 8 slightly favours the solubility of metal species.

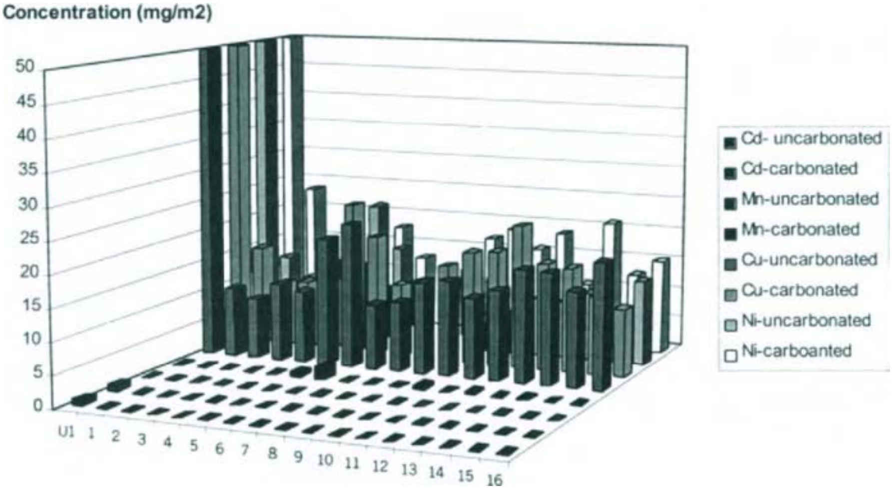

Figure 2. Heavy metals concentration (Cd, Mn, Cu and Ni) of the uncarbonated and carbonated mortars. And the limit U_1 of Netherlands Tank Leaching Test (NEN 7345).

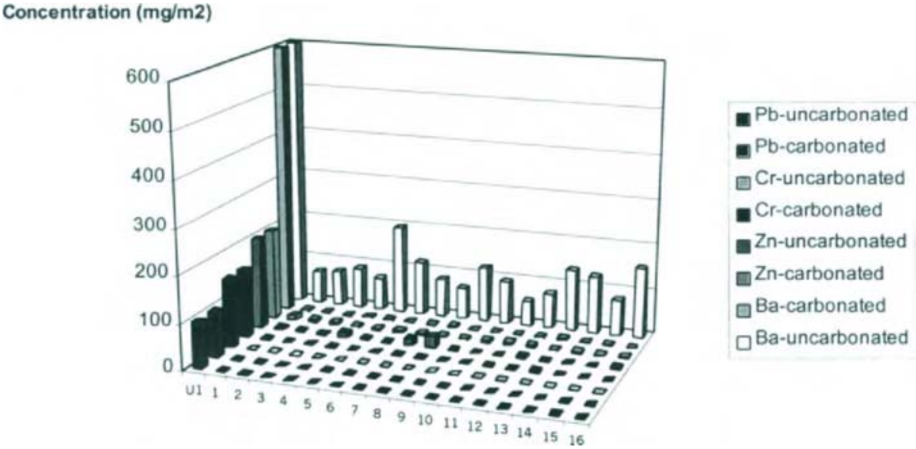

Figure 3. Metals concentration (Pb, Cr, Zn and Ba) of the uncarbonated and carbonated mortars. And the limit U_1 of NEN 7345.

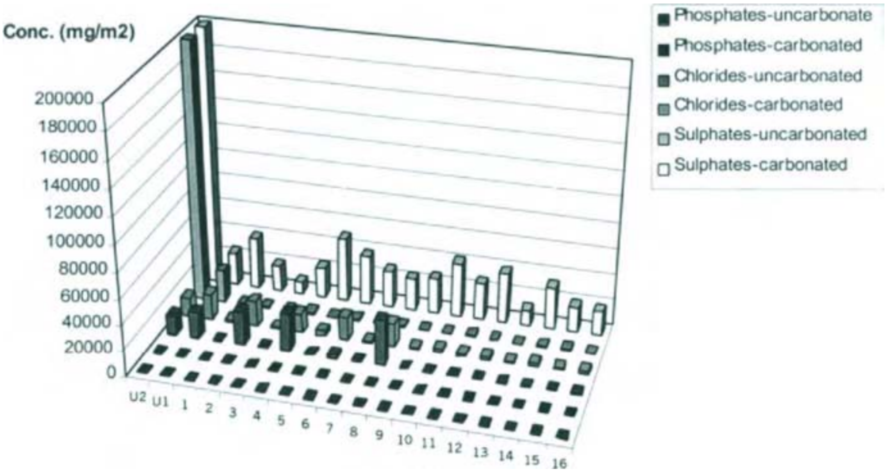

Figure 4. Accumulative leaching in carbonated and non-carbonated mortars of phosphates, chlorides and sulphates. Both limits U_1 and U_2 of Netherlands Tank Leaching Test.

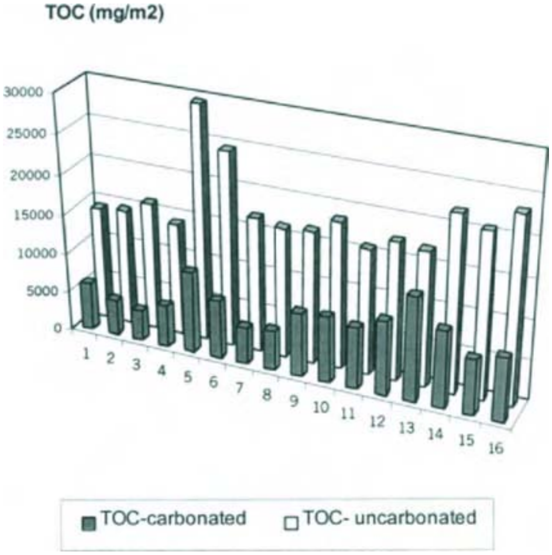

Figure 5. Accumulative leaching in carbonated and non-carbonated mortars of TOC (Total soluble organic carbon).

3. CONCLUSIONS

From the results obtained by the magnetic resonance technique (^{29}Si RNM-MAS) and the environmental assessment by the NEN-7345 leaching test, the following points are determined:

- The hydrates of the cement paste are polymerised in the samples that have undergone an accelerated carbonation process, both in the reference mortars and in the ones including sewage sludge.

-The heavy metals concentration do not exceed the U_1 limit of the Dutch standard, meaning that there is no environmental restriction for use in building. Nevertheless leaching concentration in the carbonated mortars is greater because the ettringite descompose. However, the amount of barium element leaching is much lower in the carbonated system, due to its lower insolubilisation through the formation of $BaCO_3$ and $BaSO_4$.

- The concentration of sulphates, depending on the dosage, is below the U_1 limit or between the U_1 and U_2 limits. There is no environmental restriction in either case, and treatment is required when the material's useful life is over only in the last case. However, the leaching of sulphates in all the mortars subjected to the accelerated carbonation test is greater than in the non-carbonated mortars because the ettringite undergoes a decomposition process.

-The concentration of chlorides in the eluates of the leaching process is higher due to the decomposition of Friedel's salt.

- In the accumulative leaching of all the carbonated dosages there was a large reduction in the TOC concentration, because there is an increase in the sinuousness of the porous system, and therefore a decrease in porosity.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

QUALITY CONTROL AND CERTIFICATION OF WASTE MATERIALS IN ROTTERDAM

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In this paper the experiences of quality control of secondary materials in Rotterdam are being discussed. Also the experiences of the implementation of quality control within the framework of the Dutch Building Materials Decree ('Bouwstoffenbesluit') of both raw ('primary') and waste ('secondary') materials will be presented.

1. INTRODUCTION

In the city and the port of Rotterdam, the department of Public Works is responsible for the design, construction and maintenance of infrastructural works. In the region large quantities of waste materials are being produced. Therefore, the policy was and is to stimulate the beneficial use of these waste materials (secondary building materials).
Thus Public Works has applied several types of waste materials in different infrastructural works. These materials had to meet environmental standards and had to compete with traditional building materials. Potential purchasers had to be convinced of the suitability of the waste materials and quality control was very key to this.

2. ENVIRONMENTAL ASPECTS OF WASTE MATERIALS

The applied waste or secondary materials are mainly produced as a by-product in industrial processes. They are produced by both municipality and private companies. These materials were considered by the authoroties as waste materials and therefore an environmental permit was required.
The different types of waste materials, that have been applied are:

- bottom ash (incineration of municiple waste, blast furnace)
- debris (concrete, masonry)
- soil (terrestic, sediments)
- mine tailings (mining industry)
- sieve sand (breaking of debris)

These materials are basically inert, consisting of a mineral matrix . They are slightly to modestly contaminated with heavy metals and anions . There are hardly any organic contaminants. Organic compounds are oxydated in general. The environmental risks involved with the application of these materials are mainly determined by the leaching of inorganic compounds into the soil. As a result of an increasing attention to quality control by the suppliers, the development of legislation (clear standards for content and leaching) and the establishment of quality guidelines (BRL), the environmental quality has improved. The content and leaching of contaminants has decreased (see figure 1).
As a result of research and quality control, large data sets have been collected on environmental parameters, such as content and leaching.

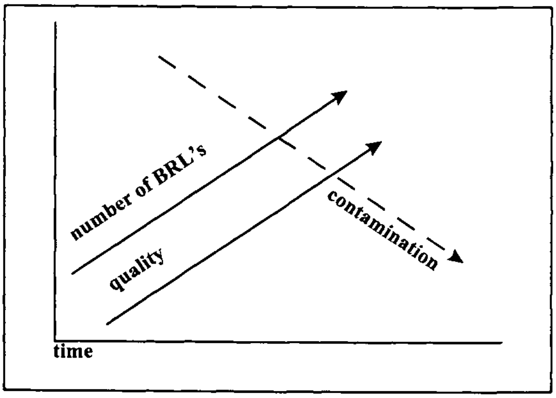

Figure 1: The influence of quality control on waste materials as a function of time

2.1 Physico-mechanical aspects of waste materials

The physico-mechanical quality of waste materials varies as the mineral structure of the materials is different. In general, the materials are coarse and the quality is comparable to traditional sand. Gemeentewerken Rotterdam uses standards, which are derived from the National Guideline, the

RAW'95. There are standards e.g. for

- grain size
- compressive strength
- durability

These standards have been laid down in each specification of an infrastructural work, that will be put out to tender. Therefore, the physico-mechanical quality of waste material is a boundary for the application in works. Quality control is based on the same tests, laid down in the RAW'95. In addition, durability tests have been developped for immobilized waste materials.

2.2 Data management

The relevant environmental data, such as content and leaching of compounds, are stored in a data base, the so-called R.I.S. (Secondary Materials Information System). This RIS has been developed by Gemeentewerken and is implemented in the local Internet information system. The information system is one of the instruments of the so-called "Active soil and building materials management concept". This concept is visualized in figure 2.
The RIS also contains physico-mechanical, commercial and practical information of the applied materials. The advantages of this information system are:

- central storage and maintenance
- data analyses
- data is available for all persons involved

2.3 Types of application

The secondary materials are applied in several infrastructural works in the city and port of Rotterdam. Subject to the grain sizes, strength and durability, they are used for different functions and types of application:

- road foundation
- sound and visual masking walls
- filling up harbours
- raw material for concrete
- raising of sites
- soil sanitation

The waste materials had to compete with conventional raw materials, which are accepted and monitored by several (mechanical) quality control systems. Due to the policy on beneficial use and the financial benefits, secondary materials became more and more accepted.
For each infrastructural work , standards are described in a specification . Physico-mechanical and environmental quality control can be combined and implemented in project management.
Contractors gain considerable financial benefits by reducing their tender price by using secondary materials and gain a competitive advantage.

2.4 Legislation

The early Dutch environmental legislation was based on the appropriate processing of waste materials (Waste Materials Act, Afvalstoffenwet). The content of contaminants had to meet standards. This was determined batch-wise. Samples were not taken according to any uniform protocol. Sampling took place at the supplier, at a temporary storage site (TSS) or at the infrastructural work.
In the nineties legislation on benificial use was based on environmental protection of the soil. Both raw and secondary materials had to meet standards for content and leaching of compounds (Dutch Buildings Material Decree, DBMD). All aspects of quality control had to be executed according to standarized Protocols (including sampling, pre-treatment,

chemical analyses, leaching), published by the Ministry of Spatial Planning and Environment (VROM).
However, already applied waste materials in Rotterdam, which are and will be recovered in reconstructions, do not always meet the present physico-mechanical and environmental standards. Landfilling of these materials, or even better, an extra treatment at a temporary storage site (TSS) is required in order to find an environmental safe solution.

2.5 Policy and Implementation of quality control

As a result of the development of legislation, the following stages of the implementation of quality control were determined:

Legislation	*Physico/mechanical*	*Content*	*Leaching*
no	batch wise	no	no
Waste Materials Act	batch wise/certification	batch wise	no/batch wise
DBMD	batch wise/certification	batch wise/certification	batch wise/certification

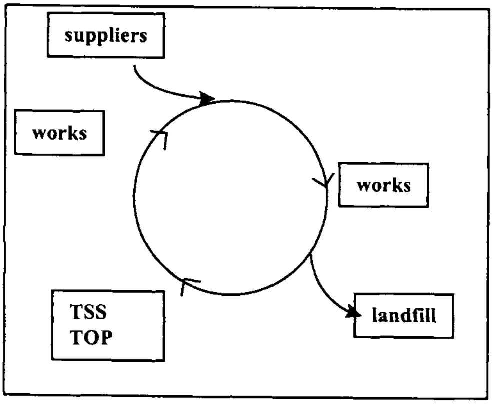

figure 2: the continuous management concept of beneficial use of secondary materials

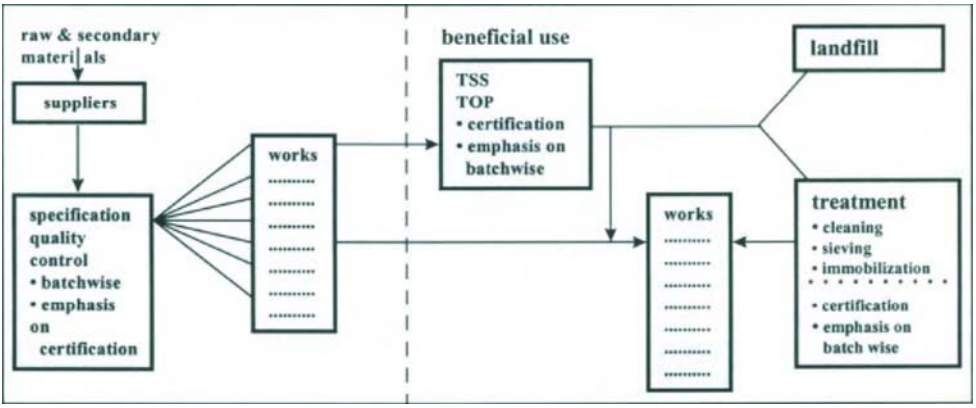

figure 3: the concept of raw and secondary
materials management and the role of quality procedures

The quality control on physico/mechanical standards was based on national publications (RAW'95). In order to optimize the control procedures, standards are laid down in quality guidelines (BRL). An independent certification organisation monitors the quality system of the supplier and the product itself. By regular surveillance audits, several raw and secondary materials have been certificated.
Beside the quality control of the materials, the management of the logistic aspects is executed by the Soil and Residue Bank (Grond en Reststoffenbank Rotterdam) which is a subdivision of Public Works. All primary working procedures are described, implemented and monitored in an ISO 9001 quality system. In the case of application of new, uniformly produced or derived materials, certification is preferable to batch-wise control. However, in case of 'older' secondary building materials, released in reconstructions, batch-wise quality control is preferable. In some cases, an extra treatment step is necessary to improve the physico-mechanical and/or environmental quality of released materials. In figure 3, the management concept is shown.

The environmental quality control has a relatively young history. However, with the implementation of the DBMD, certification of environmental quality has progressed rapidly. Procedures for environmental quality control take quit a long time, for example:

1. leaching test for granular materials (column test, NEN 7343):	4 weeks
2. leaching test for monolites (tank leaching test, NEN 7345)	10 weeks

Since the project management of infrastructural works can't afford such long procedure times, a simple and uniform quality control procedure is required. Therefore, the need for environmental certification has grown with the increasing complexity of quality control procedures. Starting in 1996, all relevant participants are still busy implementing environmental quality standards in the existing Quality guidelines (BRL's). The guidelines have to be in accordance with the goals of the DBMD.
Public Works Rotterdam, is involved in several roles in certification procedures:

- initiator of the establishment of a National Guideline (N-BRL) for soil
- expert in certification procedures (mine tailings, mswi-slags)
- members of Board of Experts
- executers of quality control in certification

As the batch-wise testing of both content and leaching is rather complex, expensive and time-consuming, the policy of Public Works is also to stimulate this type of certification. The benefits are

- simplified (cheaper and quicker) and structural quality control by an independent certification organisation
- confidence gained by both the client and the legal authoroties
- simplified procedures during the execution of the work

Certification has to be initiated by suppliers. This process is stimulated by increased cases in which the legal authorities and/or the contractor demands a certificate and/or quality procedures. They're all responsible for the implementation of a succesfull procedure. Thus, Public Works Rotterdam played and still plays an active role in this process. With the implementation of the DBMD, Public Works is about to demand certificated materials in the specifications, in case new materials are delivered by the contractor. The use of batch-wise controlled materials will mainly be accepted in reconstructions, as materials have to be reused.

In the autumn of 1999, several BRL's were established. An actual summary is published on Internet by the Stichting Bouwkwaliteit (http://www.bouwkwaliteit.nl)
As a result of delay in the national establishment of BRL, do no experience has been gained with the use of certificated secondary materials. In the summer of 2000 more experiences can be exposed and discussed. Despite the delay, certification of both raw and secondary building materials is required for a confident relation between supplier, principal and the competent authorities.

CONCLUSIONS

In summary the effects of the qualilty control process can be shown as follows:

1. Quality control of building materials is essential in engineering of infrastructural works
2. Physico-mechanical and environmental quality control can be combined and implemented in project management.
3. Quality management has lead to an improvement of the environmental quality of waste. materials and secondary materials.
4. Certification is preferable as long as the producing of the (waste or secondary) materials is uniform and conditions are controlled.
5. Applied waste materials in Rotterdam, which are recovered in reconstructions, do not always meet the present physico-mechanical and environmental standards. Batch-wise control is necessary as conditions differ.

6. Certification and batch-wise quality control are required as both new and applied secondary materials have to be managed by Public Works Rotterdam.
7. Certification has to be stimulated by both suppliers and appliers of waste materials. Public Works has an active role in this process.

Waste Materials in Construction
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Influence of the Cement Type on the Stabilisation of Fly Ashes from Municipal Solid Waste Incineration

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Municipal Solid Waste Incineration Residues (MSWIR) and specially fly ashes (MSWFA) from gas cleaning devices contain dangerous salts and toxic ions, which may be released to the environment. Therefore, fly ashes must be stabilised before their landfill. In this paper the influence of cement type on the stabilisation of MSWFA from gas-cleaning devices is presented. The cements used were, Fondu calcium aluminate cement (CAC), ordinary Portland cement (OPC) and OPC with 80% replacement by ground granulated blast furnace slag addition (OPC/BFS).

1. INTRODUCTION

This paper is a part of an extensive investigation project on Spanish municipal solid waste incineration residues (MSWIR) in which solidification/stabilisation in different cement matrices as well as new valorisation methods are being explored [1-3].

When cement materials are used as solidification/stabilisation agents of MSWIR a serious problem arises, which is related to expansion [2, 4-6).

The main source of expansion is the metal aluminium from MSWIR which is dissolved in the alkaline pore solution of matrices with liberation of H_2 gas. So the extension and kinetics of this reaction depend on the type of cement. In a recent paper Crignon et al. [4) studied this point by employing microbars of metal aluminium mixed with different kind of hydraulic binders: Portland cement, a mixture of slag and lime, and lime. The compounds of aluminium reaction (determined from DSC (Differential Scanning Calorimetry)) were: $Al(OH)_3$ and C_4AH_{13} for the three cements used. Nevertheless the kinetics of aluminium dissolution was different as a function of both the type of binder and hardening.

Auer et al. [6) investigated the hydration reactions of MSW fly ash with an experimental $C_{12}A_7/C_3A$ cement. These authors concluded that reactive calcium aluminates could be a suitable method for the immobilisation process of SO_4^{2-}, Cl^- and a wide range of toxic wastes.

The present work deals with the influence of the type of cement on the reaction of metal aluminium of fly ash from cleaning-gas device of MSWIR, the identification of the new phases formed and related expansion effects. The efficiency of matrices to stabilise the minority toxic elements and dangerous salts was also studied.

The cements used were ordinary Portland cement (OPC), a mixture of OPC and ground granulated blast furnace slag (OPC/BFS) in a proportion of 20/80, and Fondu calcium aluminate cement (CAC). The identification of solid phase was carried out by X-ray diffraction, porosity and pore-size distribution of matrices were evaluated by means of mercury intrusion porosimetry and the degree of stabilisation of minority toxic elements and dangerous salts, through analyses of extracted matrix pore solutions.

2. EXPERIMENTAL PROCEDURE

The chemical composition, concentration of minority toxic elements and X-ray diffraction analyses of the starting materials are given in Table 1 and Figs. 1 and 2, respectively.

Mixtures of cements and MSWFA were prepared at a MSWFA to cement ratio of 60:40. Matrices were fabricated with de-mineralized water at a water to solid ratio of 0.6, and stored in sealed plastic cylinders at 100% relative humidity and 21°C up to 28 days. The stabilisation of minority toxic metals and dangerous salts contained in the MSWFA was evaluated from analyses of the matrix pore solutions which were extracted by applying high mechanical pressure (500 MPa).

The elements analysed were: Cl^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}. The pH and conductivity were also measured. The concentration of Na^+, K^+ and Ca^{2+}, was determined by atomic absorption spectroscopy, Cl^- and SO_4^{2-} by automatic titration against $AgNO_3$ and by gravimetric method respectively, and those of Cd^{2+}, Pb^{2+} and Zn^{2+} by Anodic Solution Voltamperometry (ASV).

The microstructure and mineral characterisation of matrices were studied by mercury intrusion porosimetry (MIP) (Model 9320 pore Sizer Micromeritics Instrument Corp., Norcross, GA) and X-ray diffraction (XRD) patterns were recorded with a diffractometer (Model PW-1730 Philips Research Laboratories, Eindhoven, The Netherlands) using a graphite monochromator and Cu $K\alpha_1$ radiation.

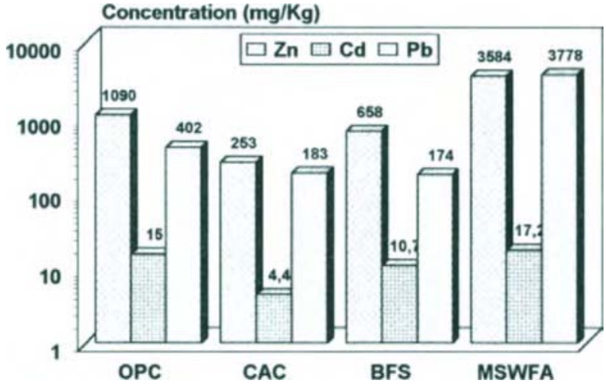

Figure 1. Concentration of Minority Elements of Starting Materials

Table 1
Chemical Composition of Starting Materials (% by weight)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	Cl^-	S^{2-}	LOI	IR
OPC	65.3	20.1	5.3	2.9	1.3	3.1	0.2	1.0	ud	-	1.5	0.8
CAC	38.3	3.5	41.2	15.3	0.4	>0.1	0.1	0.1	ud	-	0.4	0.9
BFS	40.2	37.6	12.5	1.2	8.2	-	0.2	0.6	ud	1.2	1.4	0.8
MSWFA	44.9	11.4	11.3	1.1	1.9	3.9	2.1	1.9	13	-	17.6	0.1

LOI = loss on ignition; IR= insoluble residue; (-)= unanalysed; (ud) = undetectable

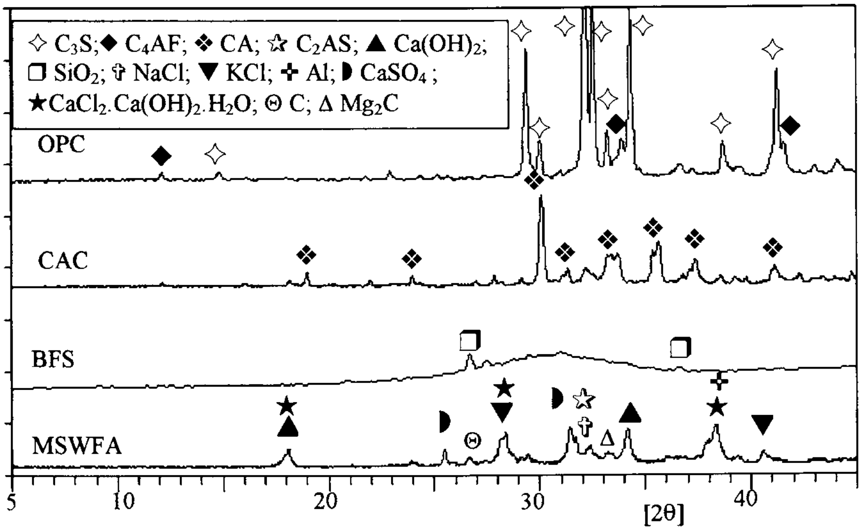

Figure 2. X-Ray Diffraction Patterns of Starting Materials

3. RESULTS AND DISCUSSION

3.1. Matrix Pore Solution

Analyses of matrix pore solutions, extracted after 28 days from mixing, appeared in Table 2. As shown, when matrices contained the MSWFA the pH decreased: from 13.14 for OPC to 11.67 for OPC/MSWFA and from 12.61 for OPC/BFS matrix to 11.52 for OPC/BFS/MSWFA one. This pH depletion is due to both a dilution effect which is caused by the replacement of 60% of cement by MSWFA and the precipitation of hydroxide phases which combined OH^- ions. In contrast, the pH of the pore solution of CAC matrix increased slightly in the presence of the MSWFA (from 12.34 to 12.41).

Table 2.
Analyses of Matrix Pore Solutions after 28 days from mixing

Matrix	pH	σ	Cl^-	SO_4^{2-}	Na^+	K^+	Zn^{2+}	Cd^{2+}	Pb^{2-}	$V^{(1)}$
		(mS/cm)	(mole/Liter)				(ppm)			(cm^3)
OPC	13.14	55	ud	0.025	0.055	0.42	5.7	0.0008	0.24	24.8
OPC/MSWFA	11.67	91	2.8	0.013	1.34	0.89	0.56	0	4.2	29.6
OPC/BFS	12.61	22	ud	0.037	0.03	0.07	0.74	0.021	0.13	21.3
OPC/BFS/MSWFA	11.52	81	2.6	0.037	1.2	0.67	0.78	0.0094	7.8	25.4
CAC	12.34	7	ud	0	0.028	0.024	44.5	0.9	0.8	22.6
CAC/MSWFA	12.41	74	1.1	0.018	0.85	0.39	27.3	0.7	5.8	33.8

(1)V= volume of pore solution (cm^3/100 g of anhydrous mixture); ud = undetectable

Nevertheless, the effect introduced by the MSWFA on the conductivity is opposite: conductivity values increased strongly. This increase is attributed to the dissolution of salts coming from the MSWFA, mainly NaCl and KCl. In fact, sodium, potassium and chloride concentrations in the pore solution increased markedly.

With respect to the minority toxic elements, concentrations of Zn^{2+} and Cd^{2+} of pore solutions are higher for OPC, OPC/BFS and CAC matrices without MSWFA. In the presence of MSWFA, it seems to be that the OPC matrix is the more efficient to immobilise Zn^{2+}, Cd^{2+} and Pb^{2+}.

The volume of the pore solution (V) is a parameter necessary to know the inner dilution effect that MSWFA or any addition may introduce and consequently alter the true concentration of ionic species. Concentration changes resulting from the different volumes of pore solutions can be separated by evaluating the quantity of any ion (m_d) in the pore solution by the equation $m_d=cV$, where c is the measured concentration of the pore solution and V the volume of the pore solution (in cm^3).

In the present work, the volume of pore solution has been calculated, from bound water content, as follows: (1) samples in powder form were dried at ambient temperature in desiccators with silica gel, up to a constant weight to eliminate the evaporable water, and (2) the samples so dried were heated from ambient temperature to 1000°C in a dynamic nitrogen atmosphere (TG curves). The bound water was represented by the weight loss observed in the TG curves, from 25°C to 1000°C. Weight loss corresponding to CO_2 and NaCl volatilisation, if present, was not considered. The volume of pore solutions is the difference between mix water and bound water.

So, to evaluate with more rigour the efficiency of matrices to stabilise any ionic species it is necessary to know the percentage dissolved in the pore solution (Table 3 and Fig. 3).

As can be seen in Fig. 3 the percentage of total chloride dissolved in the pore solution is higher in the case of the OPC/MSWFA matrix: 38% versus 30% and 17% for OPC/BFS/MSWFA and CAC/MSWFA, respectively. The lowest value of dissolved chloride in the case of CAC/MSWFA matrix is due to the high ability of combine chloride, as the XRD results showed. Similar trend in behaviour is observed for alkaline Na+K ions: 84% are dissolved in the pore solution of OPC/MSWFA matrix versus 68% and 60% for OPC/BFS/MSWFA and CAC/MSWFA. In the case of sulphate its behaviour is opposite; the OPC/BFS/MSWFA dissolves higher amount of sulphate than OPC/MSWFA one (3% and 0.9% respectively). As far as the minority toxic elements is concerning both OPC/MSWFA and OPC/BFS/MSWFA matrices immobilise Zn^{2+}, Cd^{2+} and Pb^{2+} ions, as manifested their very low percentage values (Fig. 3). Percentages of Zn^{2+}, Cd^{2+} and Pb^{2+} dissolved in the pore solution of CAC matrix without MSWFA are the highest. Nevertheless, in the presence of MSWFA the percentages decreased strongly.

Table 3.
Total (M_o) and dissolved (m_d) amount of ions in the pore solution

			OPC	OPC/ MSWFA	OPC/BFS	OPC/BFS/ MSWFA	CAC	CAC/ MSWFA
Cl^-	M_o	(g/100g)	0	7.8	0	7.8	0	7.8
	m_d		ud	2.94	ud	2.34	ud	1.3
SO_4^{2-}	M_o		3.7	4.3	0.74	3.1	0	2.8
	m_d		0.06	0.037	0.076	0.090	0	0.058
(Na^++K^+)	M_o		0.98	2.3	0.44	2.0	0.16	1.95
	m_d		0.44	1.94	0.073	1.37	0.036	1.17
Zn^{2+}	M_o	(mg/100g)	109	259	74	245	25.3	225
	m_d		0.14	0.017	0.016	0.02	1.0	0.92
Cd^{2+}	M_o		1.5	1.6	1.2	1.5	0.44	1.2
	m_d		2.0e-05	0	4.5e-04	2.4e-04	0.020	0.024
Pb^{2+}	M_o		40.2	243	22	236	18.3	234
	m_d		0.006	0.012	0.0028	0.198	0.018	0.20

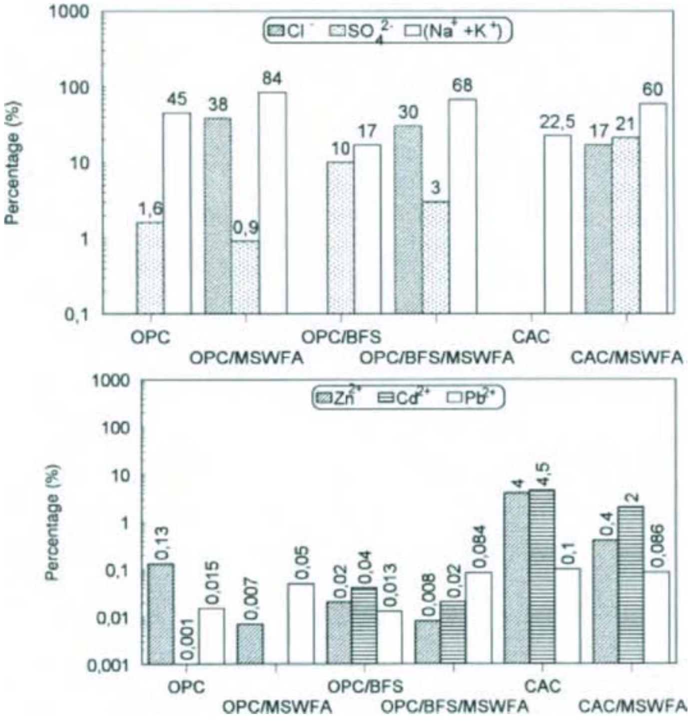

Figure 3. Percentages of Ions Dissolved in the Pore Solution

3.2. Porosity and Pore-Size Distribution

Total porosity and percentage of pores of diameter >0.05μm and <0.05μm of matrices appeared in Fig. 4. Analyses were made in small cubic pieces (1cm^3) which were previously degasified at vacuum for 15 minutes.

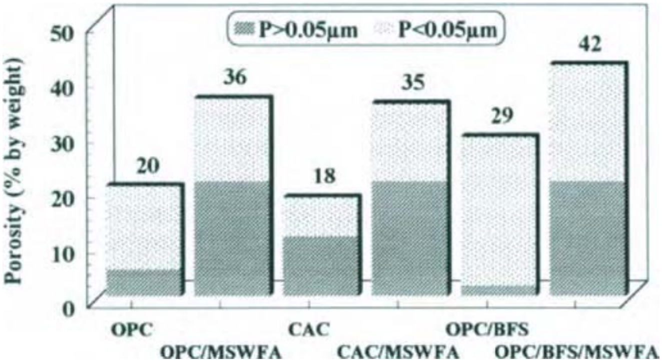

Figure 4. Porosity of Matrices

In the absence of MSWFA, the OPC/BFS matrix has the highest total porosity 29% and the highest amount of fines porous (<0.05μm) 29 %. This is due to the BFS activity which produces a great amount of gels and in consequence a refinement of the porous microstructure.

The CAC matrix is the one of lowest porosity (18%) but it has the highest amount of big pores (>0.05μm).

In the presence on MSWFA the porosity of matrices increased markedly and specially the amount of pores of diameter >0.05μm. That increase is higher than the one due to the dilution effect introduced by the MSWFA addition (60%) with the exception of OPC/BFS/MSWFA matrix. So the relative increase of porosity is 82%, 94% and 41% for OPC/MSWFA, CAC/MSWFA and OPC/BFS/MSWFA, respectively.

This increase of porosity is related to an expansion effect which is caused by the MSWFA. The metallic Al of the MSWFA is dissolved during mixing and a great amount of H_2 gas is liberated. A part of the gas is trapped in the matrix leading to the formation of big pores.

In the case of OPC/BFS/MSWFA matrix, the electrical re-dox potential of the BFS seems to inhibit partially the oxidation of Al, and, therefore, the expansion is unfavoured. Besides, the lowest pH value of that matrix plays an important role related to the kinetics of Al dissolution.

3.3. X-Ray Diffraction

X-ray diffraction patterns of hydrated matrices in the absence and in the presence of MSWFA appeared in Figs. 5 and 6, respectively. The BFS produces a strong decrease of portlandite reflections (compared diffractogram (a) and (b) in Fig. 5). The crystalline hydrated phases detected in the case of CAC matrix are: the hexagonal CAH_{10} and C_2AH_8 and the cubic C_3AH_6. The presence of the cubic C_3AH_6 indicates that "conversion" has taken place probably due to the high water to cement ratio used (0.6). This conversion produces the increase of big pores showed in Fig. 4.

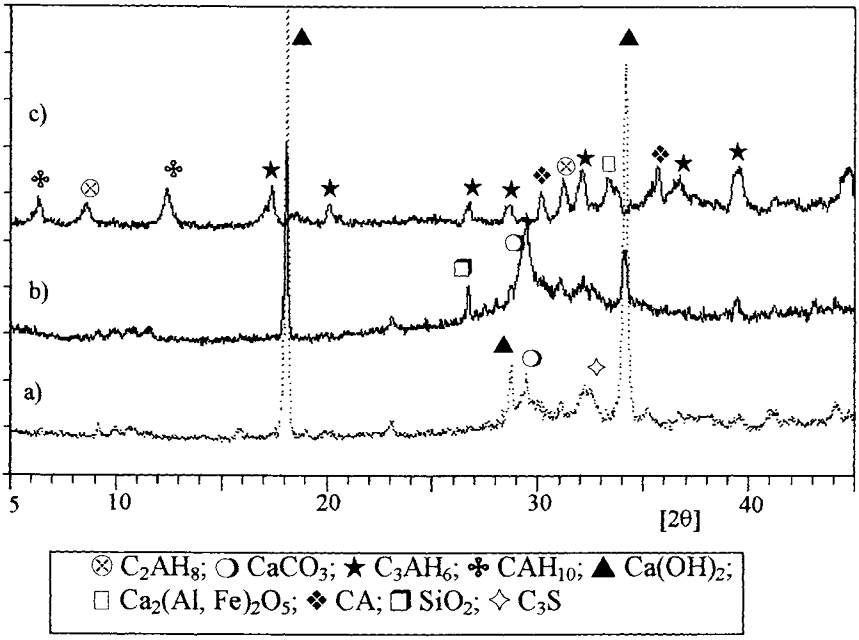

Figure 5. X-Ray Diffraction Patterns of Hydrated: a) OPC, b) OPC/BFS and c) CAC

The effect introduced by the MSWFA is clear (Fig. 6). Two new crystalline phases are detected in the three kind of matrices: $Ca_2Al(OH)_7.3H_2O$, and $Ca_2Al(OH)_6Cl.2H_2O$, whose reflection intensities increased almost proportionally to the alumina content of the matrix (see Table 1).

These new phases are formed due to both the alkalinity of pore solutions and the metallic aluminium of MSWFA. The Al dissolution produces $Al(OH)_4^-$ species which lead to the hydroxide $Al(OH)_3$ precipitation. In our case a mix (Al,Ca) hydroxide hydrate. Besides, this mix hydroxide can trap chloride ions from pore solution via OH^-/Cl^- exchange leading to the $Ca_2Al(OH)_6Cl.2H_2O$ precipitation.

In this way, hydrated CAC combined the highest amount of chloride avoiding the hexagonal CAH_{10} to cubic C_3AH_6 conversion, what is in accordance with the pore solution results where the percentage of chloride dissolved was the lowest (17%). The reflections of NaCl and KCl from the MSWFA remained in the OPC/MSWFA matrix (Fig. 6(a)). Sulphates from MSWFA combined as ettringite ($C_6As_3H_{32}$) in the three matrices. Gehlenite ($Ca_2Al_2SiO_7$) reflections from MSWFA remain practically unchanged.

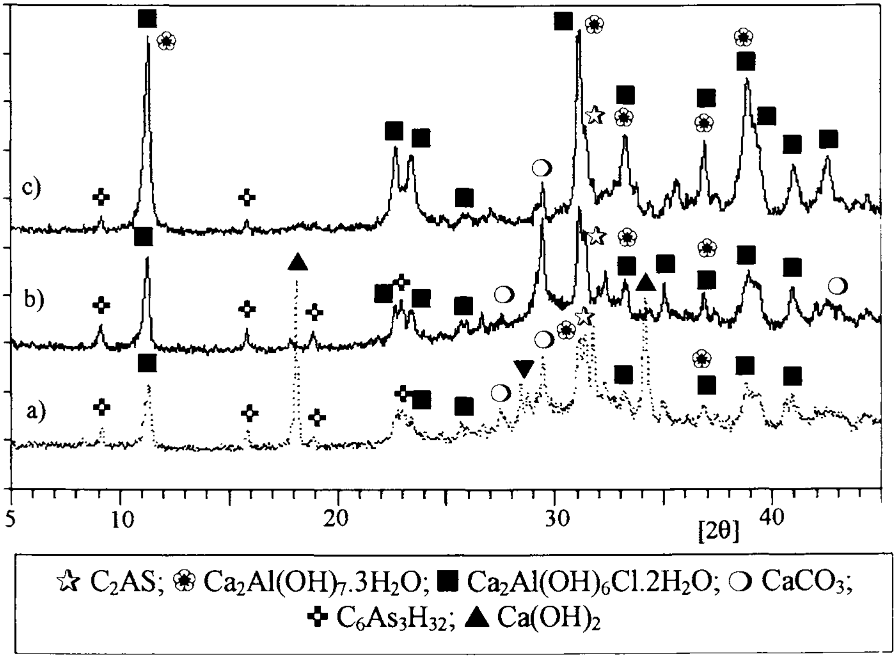

Figure 6. X-Ray Diffraction Patterns of Hydrated: a) OPC/MSFWA, b) OPC/BFS/MSWFA and c) CAC/MSFWA

4. CONCLUSIONS

1. The metallic aluminium of MSWFA causes a great expansion of cement matrices, due to its dissolution in the alkaline pore solution and H_2 gas liberation. The relative expansion or associated increase of porosity is much less marked for OPC/BFS matrix. This is due to both the lower pH values of its pore solution and the electrical redox potential of the BFS which inhibited partially the aluminium oxidation.
2. As a consequence of the metallic aluminium dissolution a new crystalline phase precipitated: $Ca_2Al(OH)_7.3H_2O$ or $2Ca(OH)_2.Al(OH)_3.3H_2O$ which partially trapped chloride to form: $Ca_2Al(OH)_6.Cl.2H_2O$
3. These phases are favoured in the case of CAC/MSWFA matrix, avoiding the hexagonal CAH_{10} to cubic C_3AH_6 conversion and leading to the lowest percentage value of chloride dissolved in the pore solution.
4. Minority toxic metals Zn^{2+}, Cd^{2+} and Pb^{2+} are strongly retained in the two OPC and OPC/BFS/MSWFA matrices as their pore solution analyses revealed.

ACKNOWLEDGEMENT

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Hydrothermal Treatment of Fly Ash from Municipal Solid Waste Incineration

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The effect produced by hydrothermal treatment of fly ashes from municipal solid waste incineration (MSWFA) is discussed in this work. The more interesting results showed that practically 100% of chloride and metal Al from the fly ash are dissolved. CSH gel and katoite (C_3ASH_4) are the main cemented hydrated phases formed after 1 hour of hydrothermal treatment.

1. INTRODUCTION

From a sustainable development point of view, the limitation of waste production and the re-use of waste materials are two of the objectives to be developed in the new millennium. A wide range of wastes are being re-used in construction materials. That is the case of bottom and fly ashes and slags from incineration of municipal solid wastes [1-9). Nevertheless, the re-use of this kind of wastes in construction causes serious problems which are mainly related to soluble chloride and metal aluminium contained in them.

MSW fly ashes (MSWFA) have to be treated prior to its incorporation in construction. Nzihou and Sharrock [10) developed a phosphate chemical treatment of MSWFA in an aqueous sol-gel process in which chlorides were extracted and hydroxylapatite precipitated. MSWFA was then calcinated in an air atmosphere at 900°C. Vaquier et al. [11) developed a process which was based on an exhaustive washing of MSWFA followed by a phosphatation and calcination at 750°C.

In this work the hydrothermal treatment of MSWFA was studied as a new way to convert MSWFA as a valuable resource. The new hydrated phases formed also have the potential of immobilising another ionic species and can also serve as precursors of new type of low-energy-cements. The experimental methodology was based on previous works carried out by the authors on fly ashes from coal combustion [12,13).

2. EXPERIMENTAL PROCEDURE

MSWFA from cleaning-gas devices was mixed with de-mineralised water at a water to MSWFA ratio of 10. The mixture was hydrothermally treated at 200°C and 1.24 MPa pressure for periods of 1h, 2h, 4h and 6 hours. The evolution of the liquid phase with time of hydrothermal treatment was followed by means of: pH, conductivity, chloride, sulphate and minority zinc, cadmium and lead concentration measurements.

The hydrothermal treatment was carried out with a Parr Mod. 4522 pressure reactor equipment (1000 mL pump with split-ring closure and a PID Mod. 4842 temperature controller). Changes of fly ash composition were characterised by X-ray diffraction (XRD), infrared spectroscopy (IR) and thermal analyses (TGA) and (DTA). X-ray diffraction (XRD) patterns were recorded with a diffractometer (Model PW-1730 Philips Research Laboratories, Eindhoven, The Netherlands) using a graphite monochromator and Cu $K\alpha_1$ radiation, IR study was carried out on a Perkin Elmer 783 instrument and KBr pellets containing 0.5% of sample. Thermal analyses were recorded with a Netzsch equipment with STA 409 simultaneous analysis system using 50 mg samples and a dynamic nitrogen stream (flow rate = 100 cm^3/min) at a heating rate of 10°C/min.

The chemical composition of starting municipal solid waste fly ash is given in Table 1.

Table 1.
Chemical Composition of Starting Municipal Solid Waste Fly Ash (MSWFA) (% by weight)

CaO	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**SO_3**	**Na_2O**	**K_2O**	**Cl^-**	**Zn^{2+}**	**Cd^{2+}**	**Pb^{2+}**	**LOI**	**IR**
44.9	11.4	11.3	1.1	1.9	3.9	2.1	1.9	13	0.36	0.0017	0.38	17.6	0.1

LOI = loss on ignition; IR= insoluble residue

3. RESULTS AND DISCUSSION

3.1. Characterisation of Liquid Phase

The evolution of liquid phase composition with time of hydrothermal treatment appears in Table 2. The ions analysed were Cl^-, SO_4^{2-}, Zn^{2+}, Cd^{2+} and Pb^{2+} as well as pH and conductivity. Values of starting MSWFA (time 0) have been included in this Table for comparison. The units of measured concentrations in the liquid have been converted in g per kg of MSWFA by the equation $m_d = cV$, where c is the measured concentration of the liquid and V is the volume used (150 cm^3).

Table 2.
Concentration of Elements dissolved during the Hydrothermal Treatment of MSWFA

Time	Cl^-	SO_4^{2-}	Zn^{2+}	Cd^{2+}	Pb^{2+}	pH	σ
(hours)	(g/Kg MSWFA)						(mS/cm)
0[1]	130	46.8	3.6	0.017	3.8	-	-
1	128	0.60	0.0086	0	0.075	12.08	27.4
2	130	0.12	0.0072	0.00013	0.123	12.07	27.0
4	130	0.60	0.0054	0.00011	0.199	12.09	27.4
6	130	0.12	0.0047	0.00021	0.045	12.15	27.3

[1] Time 0 is before the hydrothermal treatment

As shown in Table 2, a plateau of stabilisation is produced after 1 hour of treatment for chloride, pH and conductivity (σ). Chloride reached concentration values close to that of starting MSWFA, what indicates its total dissolution. The pH stabilised at a value of about 12.1, and conductivity at 27 mS/cm. The concentration of minority Pb^{2+} increased progressively during the first 4 hours decreasing thereafter, nevertheless Zn^{2+} decreased after 1 hour. Cd^{2+} concentration is very low increasing after 6 hours of treatment.

In Fig. 1 the percentages of ions dissolved with time of hydrothermal treatment is presented. As can be seen, the percentages of SO_4^{2-}, Zn^{2+}, Cd^{2+} and Pb^{2+} dissolved are considerably lower than those of Cl^-. In general, Zn^{2+} reached the lowest values whereas Pb^{2+} reached the highest. Probably, the minority toxic elements and sulphates are incorporated in the new hydrated phases formed as a result of the MSWFA hydrothermal treatment.

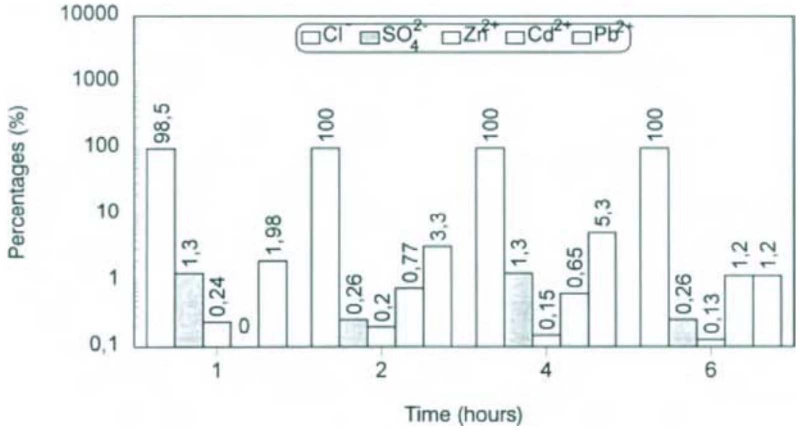

Figure 1. Percentages of Ions Dissolved in the Liquid Phase

3.2. Characterisation of MSWFA After Hydrothermal Treatment

3.2.1 X-Ray Diffraction

The main crystalline compounds of the untreated MSWFA (Fig. 2(a)) are the follows: NaCl (alite), KCl (sylvite), $CaCl_2.Ca(OH)_2.H_2O$, $CaSO_4$ (anhidrite), $Ca(OH)_2$ (portlandite), $CaCO_3$ (calcite), $Ca_2Al_2SiO_7$ (gehlenite), Fe_2O_3, SiO_2 (α-quartz), Al and probably C and Mg_2C.

After 1 hour of hydrothermal treatment (Fig. 2(b)) all the X-ray reflections of chloride-compounds disappeared, what suggest that they have been dissolved as the analyses of liquid showed, where the concentration of chloride represents the 100% of total amount of chloride of starting MSWFA.

Al reflection at 38.4 of 2θ angular zone disappeared, what indicates its dissolution which is favoured by the high pH (12.1) of the liquid (Fig. 1). In fact, the liberated H_2 gas was clearly observed as a result of hydrothermal treatment. Nevertheless, neither $Al(OH)_3$ nor $Al(OH)_3.2Ca(OH)_2.H_2O$ were formed. The later mix Al, Ca hydroxide hydrate was detected, when the MSWFA was mixed with cements [14]. Probably dissolved Al combined as $Ca_3Al_2(SiO_4)(OH)_8$ (C_3ASH_4). This new hydrated phase (cubic crystallographic variety of hydrogarnet series) appeared with intense reflections and was also formed during the hydrothermal treatment of fly ashes from coal combustion as a result of the fly ash pozzolanic reaction with CaO [12].

Anhidrite ($CaSO_4$) is transformed in $CaSO_4.0.6H_2O$ and the intensity of gehlenite (C_2AS) reflections and portlandite (CH) remains unchanged through the treatment. The $Ca_{1.5}SiO_{3.5}.xH_2O$ (called CSH gel) appeared although its reflections are overlapped with those of calcite, but it was confirmed from IR analyses by the strong absorption band at 950 cm^{-1}.

As was mentioned in the introduction, chloride and metallic aluminium of MSWFA represent the main problems from the point of view of its potential valorisation towards construction materials. The hydrothermal treatment of MSWFA avoids such problems and in addition new hydraulic phases are formed: C_3ASH_4 and $Ca_{1.5}SiO_{3.5}.xH_2O$. These phases have the property of incorporating a wide range of species via solid solution mechanism, in the case of katoite silicaton, and via intercalation for $Ca_{1.5}SiO_{3.5}.xH_2O$, providing, therefore, stabilisation mechanisms for minority toxic elements of MSWFA.

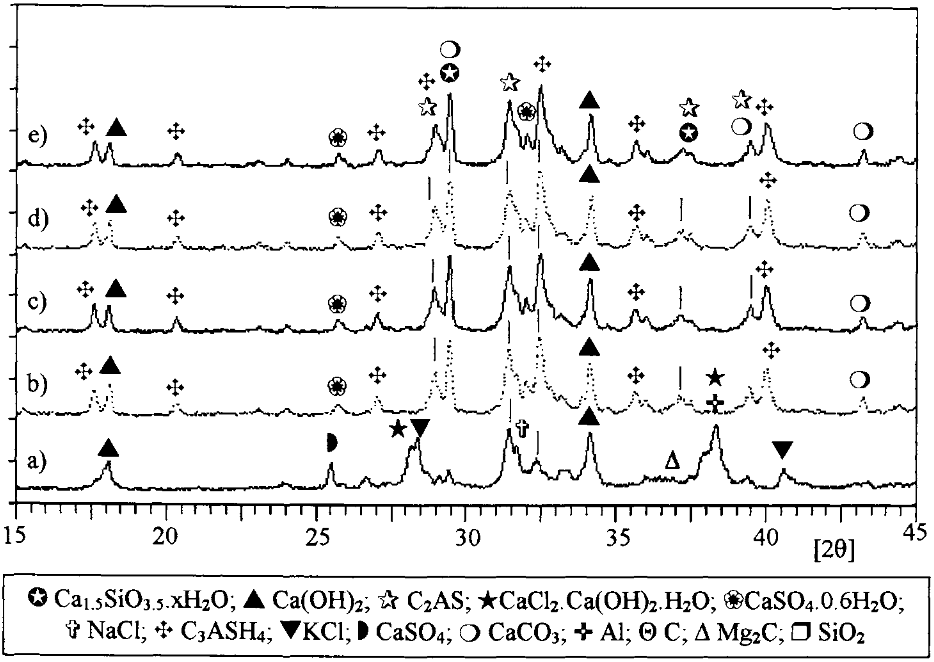

Figure 2. Evolution of X-Ray Diffraction Patterns of MSWFA with time of Hydrothermal Treatment: (a) untreated; (b) 1hour; (c) 2 hours; (d) 4 hours and (e) 6 hours.

3.2.2 Thermal Analyses

TGA and DTA curves of MSWFA before and after 1 hour of hydrothermal treatment appear in Fig. 3. As XRD and liquid solution analyses showed, from 1 hour to 6 hours of treatment, a plateau of stabilisation was produced. Therefore, for the rest of characterisation studies we have chosen those obtained for 1 hour.

In the case of untreated MSWFA (Fig. 3(a)), a weight loss is produced in the TG curve between 390°C and 600°C, with an inflection at 470°C. In the corresponding DTA curve two endothermic effects appeared at 425°C and 500°C, which could be related to the release of water from portlandite ($Ca(OH)_2$) and $CaCl_2.Ca(OH)_2.H_2O$. Between 600°C and 800°C another weight loss is detected which could be due to decomposition of calcite ($CaCO_3$) and combustion of coal. In this range of temperature the two endothermic peaks at 690°C and 750°C could be attributed, the first to metallic aluminium fusion and the second to CO_2 releases. The weight loss observed from 800°C is due to the volatilisation of NaCl.

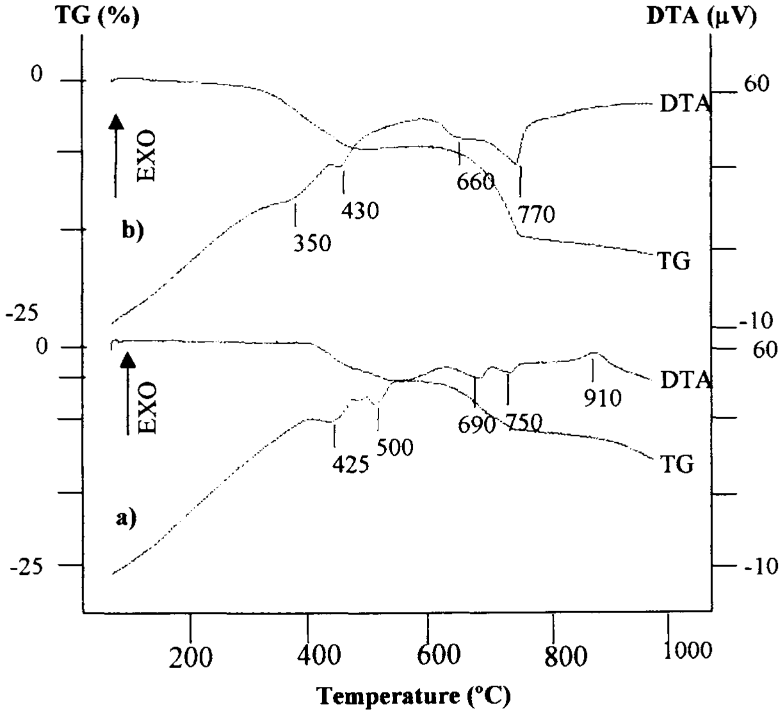

Figure 3. TGA and DTA curves of MSWFA: (a) untreated; (b) after 1 hour of Hydrothemal Treatment

After 1 hour of hydrothermal treatment (Fig. 3(b)) the main changes are: the absence of the NaCl volatilisation (no weight loss is produced from 800°C); the first weight loss is shifted to lower temperature values (270°- 460°C) and the weight loss corresponding to

$CaCO_3$ decomposition is considerably higher. The content of combined water is 7.6% and that of $CaCO_3$ 17.5% (by unheated sample).

3.2.3 Infrared Spectroscopy Analysis

In the case of untreated MSWFA (Fig. 4 (a)), an intense absorption band appeared between 3000 cm^{-1} and 4000 cm^{-1} with three maxima at 3660 cm^{-1}, 3580 cm^{-1} and 3460 cm^{-1}, which correspond to the lattice water and OH^- group vibrations. After one hour of hydrothermal treatment (HT) (Fig. 4 (b)) the maximum at 3660 cm^{-1} increased strongly, as well as the absorption bands of calcite ($CaCO_3$) at 1460 cm^{-1}, 880 cm^{-1} and 720 cm^{-1}. Between 1100 cm^{-1} and 800 cm^{-1} a strong new band appeared centred at 950 cm^{-1}, which is related to $[SiO_4]^{4-}$ vibration from the $Ca_{1.5}SiO_{3.5}.xH_2O$. The absorption band at 1130-1160 cm^{-1} is due to sulphate group from anhidrite.

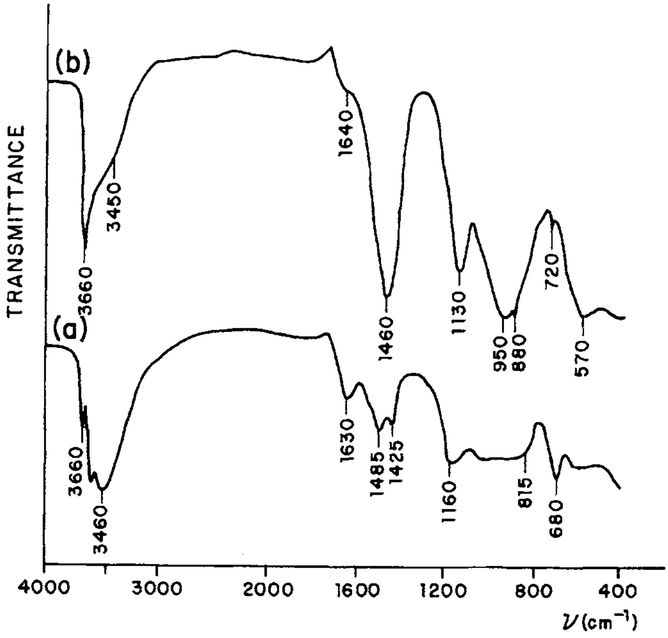

Figure 4. IR Analysis of MSWFA: (a) untreated; (b) after 1 hour of Hydrothemal Treatment

4. CONCLUSIONS

1. The hydrothermal treatment is an useful way to dissolve chloride and metallic aluminium of MSWFA. So, MSWFA can be treated as a valuable resource.
2. New hydraulic phases were formed: katoite silicaton: $Ca_3Al_2(SiO_4)(OH)_8$ and $Ca_{1.5}SiO_{3.5}.xH_2O$. Both have the capacity of immobilising toxic ionic species by two

differentiated mechanisms: via solid-solution in the case of katoite and via intercalation in the interlayer space for $Ca_{1.5}SiO_{3.5}.xH_2O$.
3. These phases were also formed during a similar hydrothermal treatment of fly ash from coal combustion and CaO, and can serve as precursors of new type of cements.

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G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

PVC AND PET PLASTICS TAKEN FROM SOLID URBAN WASTE IN BITUMINOUS CONCRETE

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In recent years a shortage of natural resources for building transportation infrastructures urged the development of innovative technologies in the field of waste materials deriving from industrial manufactures or domestic use.

This study attempts to give a contribution to the recycling of plastics deriving from solid urban wastes (Refuse Derived Plastics - RDP) in bituminous concrete.

In particular, this research refers to the use of low degradable plastics, hard and non-mixable with bitumens (PVC and PET), as a possible replacement of a portion of the stone aggregate mixture.

The aim was to find a way of reusing waste plastics in order to reduce their volumes in refuse disposal sites and at the same time to reduce the amount of inerts drawn from quarries, which often lead to environmental problems.

In the first phase of the research, already carried out by the authors, the limits of this application were defined, as well as the best conditions of use of the above mentioned plastics by means of the traditional mechanical and rheological characterization tests of bituminous concrete (Marshall Test, Indirect Tensile Test, Static Creep Test).

This paper treats the dynamic characterization of mechanical properties of bituminous concrete mixtures added with plastics.

Dynamic tests were carried out, which allowed to draw Master Curves as the percentage of plastic material used in the mixtures varied and for different test conditions.

Moreover, the fatigue behaviour of the different mixtures of bituminous concrete was analyzed.

The results obtained confirmed that it is possible to use RDP to manufacture bituminous concrete, in particular hard plastics non-mixable with bitumens, on the condition that PVC and PET are thin milled, of a small size and used in limited quantities.

1. INTRODUCTION

The possibility to employ recycled materials in different fields of building works, using the proper forms of disposal by means of compatible technologies, has always urged scholars to find new forms of employment of such disposal material.

The main purpose of these studies is to reduce both the employment of natural resources, which are usually difficult to find and not always renewable, and the amounts of waste material to dispose in waste disposal sites, with consequent environmental benefits.

This research deals with the use of plastic materials deriving from differentiated garbage collection (Refuse Derived Plastics - RDP) in bituminous concrete.

In Italy differentiated collection of domestic wastes is the main form of recovery and selection of secondary raw materials. It is approximately equal to 1,160000 tons and is 4.4% of the total amount of waste produced. In this context, on the basis of an analysis in weight, plastic materials and rubber are about 14-15% of wastes collected. About half of consumption of plastic materials consists of disposable products, whereas the remaining half belongs to the category of lasting products with more or less long life. As far as containers made of plastic materials (bottles and various types of vessels) are concerned, they are devided into PET (45%), then polyolefins (PP and PE, 35%) and finally PVC, which makes up the remaining 20% [1].

This research focuses on identifying forms of recycling of PVC and PET as they are non toxic products, which however at the moment have difficulties in being reused in the production cycle.

PVC (polyvinylchloride) is a vitreous or poorly crystalline thermoplastic material which decomposes at about 180 °C developing hydrochloric acid and then carbonizes. Density of the compact polymer ranges between 1380 - 1410 daN/m^3.

PET (polyethyleneterephtalate), instead, is an amorphous or crystalline thermoplastic material, which melts at 256 - 264 °C. Densities of amorphous and crystalline PET are about 1330 and 1455 daN/m^3 respectively [2].

It is evident that both plastics examined cannot be mixed with bitumens and therefore they are considered as inerts belonging to the mixture of the aggregates. This is confirmed by the fact that plastics themselves are low degradable and therefore long lasting in time.

The material used in this experiment was made of 45% PVC, 45% PET and the remaining 10% other types of plastics. It is always properly selected, washed and crushed.

For the first applications in the field of road construction, this type of plastics will be used in bituminous concretes for base courses and binder courses. Their use in the top layer will require further investigations in order to verify the effects on surface grip between tyre and pavement, and on the aging which they suffer due to direct contact with atmospheric agents.

2. PREVIOUS EXPERIENCE

In a previous experience developed by the authors [3] different aspects were analyzed and the best ways of employing the RDP used (PVC e PET) in bituminous concrete were defined. Such investigations were carried out in the light of the results produced by a number of conventional tests executed in accordance with what recommended by Italian (CNR) and other international regulations.

The investigations carried out are the following:

1. Control of thermic stability of plastics at the temperature of bituminous concrete manufacturing (140 - 160 °C);
2. Determination of the best way of manufacturing bitumen-aggregate-RDP mixtures;
3. Determination of the optimal particle-size distribution curve of the plastic elements;
4. Determination of the optimal particle-size distribution curve of the aggregates;
5. Determination of the way of replacing the aggregate mixture with plastics at the equivalent fraction;
6. Determination of the optimal percentage of plastics to be used in bituminous concretes;
7. Control of the effects produced by the use of plastics on the adhesiveness among bitumen-RDP-aggregate.

Point 1 was verified by executing, on the specimens of RDP used, two tests in accordance with the following standards: UNI 5637-65 "Determination of PVC thermic stability by means of the colour variation method" and ISO 182-65 "Determination of the trend of PVC compounds and PVC based products and copolymers towards freeing hydrochloric acid and other acid products at high temperatures (Congo red method)".

Points 2, 3, 4, 5 and 6 were verified by evaluating the results produced by the traditional tests on bituminous concretes (Marshall and Indirect Tensile Tests) carried out on mixtures added with RDP in different forms.

Point 7 was verified by comparing the results produced by Static Creep Tests carried out both on regular specimens and on specimens treated in water for 24 hours at 60 °C.

A brief outline of the results obtained, and therefore, of the best operation conditions, follows:

- Plastic materials used proved stable from a thermic point of view at manufacturing temperatures of hot-worked bituminous concretes. Therefore, it is correct to use them as inerts to replace some fractions of the stone aggregate mixture.
- The best way of manufacturing bituminous concretes with RDP is that in which plastics are added in the last phase of the mixing of bituminous concrete (aggregate & bitumen T=150°C + Filler & RDP T=25°C) and the mixture is completed in 3 minutes.
- The optimal particle-size distribution curve of plastic elements is that typical of fine sands, 100% passing the 1 mm sieve. A minimum amount of filler was found in it (Table 1).
- The particle-size distribution curve of aggregates which produced the best results is a typical curve of binder layer (Table 2).
- The best form of replacing the aggregate with plastics is that in weight of equivalent granulometric fractions. In this case the volume of plastics introduced is higher than the corresponding aggregate fraction replaced as density of plastics is about one half than that of the aggregates used.
- The maximum value of RDP percentage to be used in bituminous concretes is equal to 10% in weight compared to the aggregate mixture.
- Mixtures executed in the optimal conditions did not cause considerable problems in adhesiveness tests.

The characteristics of the materials used in this first experimentation are reported in Tables 3 and 4.

Table 1 – Optimal RDP mix grading

Sieve size (mm) ASTM	% Passing weight accumulated
1	100
0,42	20
0,177	6
0,074	1

Table 2 – Optimal aggregate mix grading

Sieve size (mm) ASTM	% Passing weight accumulated
25,4	100
15	83
9,52	65
4,76	45
2	32
0,42	16
0,177	10
0,074	6

Table 3 – Characteristics of bitumen

Characteristics	M/U	Value	Test Standard
Penetration 25°C, 100g, 5s	(dmm)	98	CNR n°24/71
Softening Point – Ring&Ball	(°C)	46,2	CNR n°35/73
Fraass Breaking Point	(°C)	- 16	CNR n°43/74
Viscosity (60 °C)	(cst)	120000	SNV671908
Viscosity (135 °C)	(cst)	209	SNV671908

Table 4 – Characteristics of aggregate

Characteristics	M/U	Value	Test Standard
Apparent Specific Gravity	(g/cm^3)	2,63	CNR n°63/78
Real Specific Gravity	(g/cm^3)	2,65	CNR n°64/78
Porosity	(%)	0,75	CNR n°65/78
Los Angeles Abrasion Loss	(%)	28	CNR n°34/73
Frantumation Index	(%)	139	CNR n°75/80

Finally, it should be noted that the optimal percentage of bitumen was determined by means of Marshall method.

3. EXPERIMENTAL PROGRAMME

This study develops the research in order to investigate the real possibility to use bituminous concrete mixtures added with RDP in road pavements. In particular, the purpose of this further research is to carry out an investigation on the dynamic characterization of mechanical properties and of fatigue behaviour of the mixtures themselves. In the case under discussion, it is known that the most reliable tests are the dynamic tests which simulate the real load conditions best. In this experimentation the complex modulus and fatigue tests were carried out by means of an electro-oleodynamic apparatus MTS 810, controlled by software authorized by SHRP Equipe Corporation, capable of handling the load, the application frequency and the temperature.

In this further investigation, the same materials (bitumen, aggregate and RDP) used in the first experimentation have been used as well as the best methods of use previously detected (with reference to particle-size distribution curve of aggregates and plastics, and the manufacturing criteria used for the mixtures).

Again, in the light of the results produced by the previous study, five mixtures of bituminous concrete were studied obtained by replacing, in weight, the equivalent granulometric fractions with 0-3-5-7-9 % of RDP respectively.

The procedure used for manufacturing specimens was that provided for by Marshall test according to CNR standard n°30/73.

3.1. Complex modulus tests

The dynamic characterization of mechanical properties of bituminous concrete mixtures was investigated by means of the complex modulus E* and of the phase angle φ.

In order to carry out the investigation in an adequate temperature and frequency range, the test conditions were established on the basis of the ASTM D 3497-79 (95) "Standard Test Method for Dynamic Modulus of Asphalt Mixtures" [4]; it was also considered appropriate to carry out further investigations at low temperature and high frequency.

Test temperatures were:

- 5°, 25° and 40°C [ASTM D 3497-79] ;
- -10°C [climatic conditions typical of winter time in Italy].

The specimens were conditioned in an thermostatic chamber and were left for twelve hours at the test temperature prior to testing.

The specimens were tested at the following frequencies:

- 1; 4 and 16 Hz [ASTM D 3497-79];
- 30 Hz [to simulate the strain caused by vehicles travelling at typical motorway speeds].

According to the ASTM standard, the strain applied corresponded to a sinusoidal load wave with an amplitude of 2 kN for tests at –10 °C and 5 °C, of 1 kN for tests at 25 °C and of 0.5 kN for those at 40 °C. The tests were carried out in series starting from the minimum temperature and the maximum frequency, in order to render the procedure less damaging to the specimens.

Each test lasted 45 seconds, the maximum established by the ASTM standard; data were taken between the 30th and 45th seconds, ensuring the stabilization of the deformations inside the specimens. The following data were acquired during the tests: load measurement, by means of a load cell; axial deformation, using a pair of extensometers; actuator axial shift, acquired by a transducer, and temperature, measured by means of a thermocouple placed in a sample specimen. The values obtained were registered at a rate of 100 samplings per period. Five specimens for each mixture were submitted to dynamic testing. The results were obtained by averaging the values for each separate mix.

Figure 1 shows test results; each diagram records, for the five mixtures studied, the isotherm behaviours of the absolute value of the complex modulus |E*| in connection with the different frequencies employed.

The analysis of the results proves that for temperatures such as –10 °C and 5 °C values of |E*| increase as the RDP % introduced in bituminous concrete mixtures increases. The contrary occurs for temperatures such as 25 °C and 40 °C.

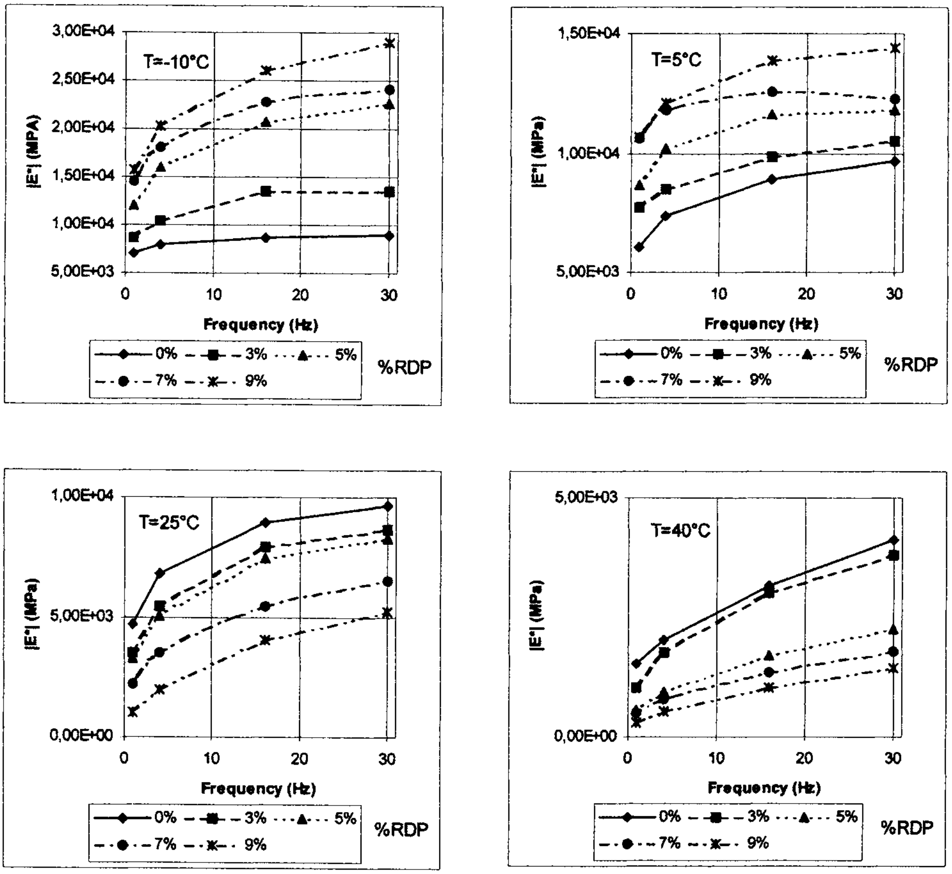

Figure 1 - The isotherm behaviours of the absolute value of the complex modulus |E*| in connection with the different frequencies employed.

This aspect proves that the use of high % of RDP renders bituminous concretes shorter to low temperatures and more ductil to high ones. In this context the fact that isotherm behaviours of mixtures made with 5% of RDP have always had a central position compared to others is emphasized.

By effecting a considerable number of tests at differing temperatures and frequencies, master curves were obtained, which are known to relate the absolute value of the complex modulus |E*| to a reduced frequency in which the effect of temperature and of stress frequency are considered simultaneously. The shift factor was calculated using the expression proposed by Verstraeten [5]. In this study, the reference isotherm was taken as that for 25 °C (298 °K); the shift factors α_T corresponding to each temperature analyzed are reported in Table 5.

Table 5 – Shift factor α_T as a function of temperature

Temperature (°C)	-10	5	25	40
α_T	46273,47	332,71	1	0,02

The analysis of the behaviour of master curves (Figure 2) shows that all mixtures manufactured with the different % of RDP feature a higher stiffness to temperature (or to load time) than the reference bituminous concrete. In fact, as the RDP % increases, an increase of the inclinations of the master curves themselves is registered.

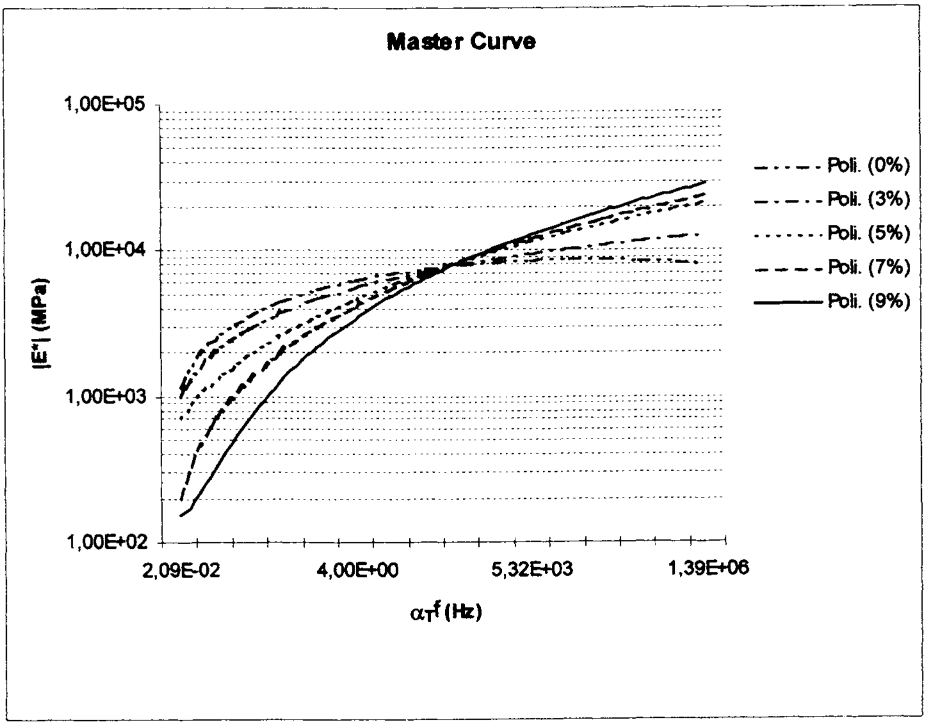

Figure 2 - Master curves of the five mixtures manufactured with the different % of RDP.

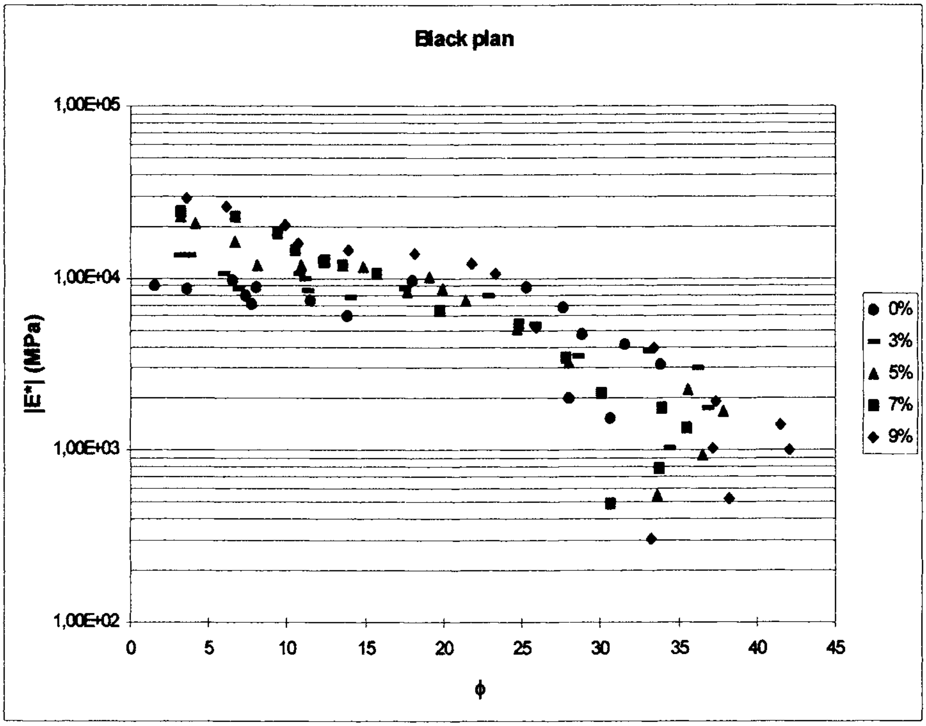

Figure 3 - Representing of the results of the complex modulus in the Black's plane (|E*|, φ).

The diagram representing the results of the complex modulus in Black's plane (|E*|, φ), shown in Figure 3, reports the simultaneous variations of the stiffness value |E*| and of the phase angle φ for the different test temperatures and frequencies. The analysis of the results suggests that the phase angle φ, that is, the viscous component of mixes, features a trend towards increasing as RDP % increases in the mixtures, for all test conditions; this aspect is even more marked in correspondence with the low values of |E*|. It also comes out that, as RDP % increases, mixes are stiffer in correspondence with low values of phase angle φ; the contrary occurs in correspondence with high values of φ.

3.2. Fatigue tests

Fatigue strength of different mixtures was determined by submitting specimens to repeated Indirect Tensile Stresses by applying an impulse type of load, according to the controlled stress method. The impulse type of load was chosen as it accurately reproduces the type of stress found in road pavement [6].

During testing load conditions were kept constant with the following application methods: duration of load impulse equal to 0,1 seconds; rest period equal to 0,5 seconds.

An only temperature was used for all testing, equal to T = 20 °C.

The traditional fatigue rupture criterion was used, according to which the material is subject to crisis when the deformation recorded during the test reaches a value twice as much the initial one ($\varepsilon_f = 2*\varepsilon_o$). The initial deformation ε_o was determined by using measurements recorded by the extensometers at the 200th cycle so as to allow the specimen to settle.

Fatigue strength of traditional bituminous concretes, for the testing method used (controlled stress), does not differ much from that in which the complete specimen rupture occurs.

Testing were carried out assigning the following stress values during load impulse: 100 kPa, 300 kPa and 400 kPa.

For each of the three stresses assigned, five specimens of each mix were submitted to fatigue testing; the results were obtained by averaging the values for each testing condition.

The experimental results obtained (shown in Figure 4) allowed to draw, for each different mixture analyzed, the Whöler diagram, which, for bituminous materials, is made of lines in a bilogarithmic co-ordinate system. The fatigue lines were determined according to the general expression $\sigma = C*N^{-b}$, where σ represents the stress, N the number of cycles, and C and b the parameters of the lines.

The analysis of the results suggests that as the RDP % increases, the number of cycles (N) decrease. In other words, as it may be expected the presence of plastics (PVC and PET) reduces the fatigue strength of bituminous concretes.

Moreover, it was found that, in correspondence of higher stresses (400 kPa), the number of cycles which bring the material to rupture feature very limited values and drop drastically as the RDP % increases. In correspondence with low stresses (100 kPa), instead, the number of cycles tend to have higher values, which may be considered acceptable for the operating life required for road pavements.

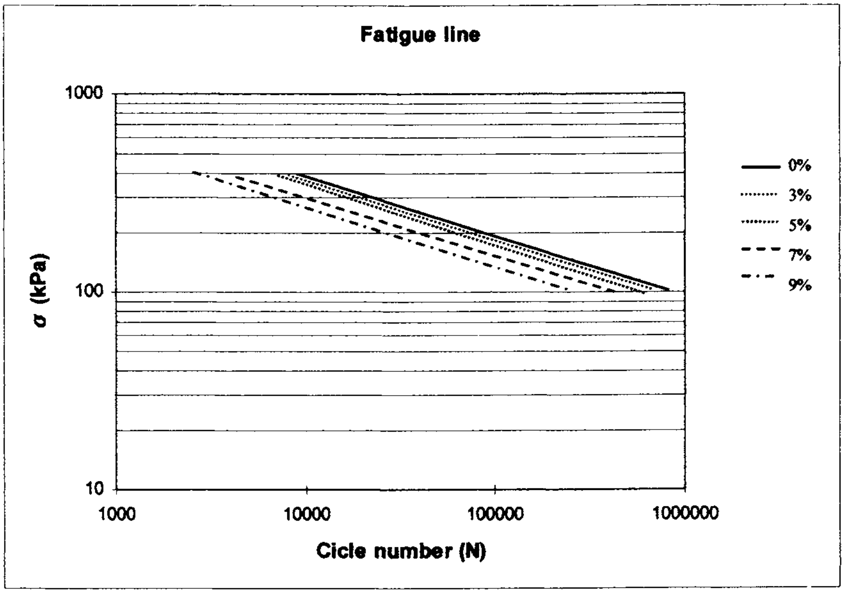

Figure 4 - Representing of the results of the fatigue lines in the Whöler diagram.

All things considered, therefore, the mixtures analyzed may be used in binder (with limited % of RDP) and base courses (with RDP % not exceeding 10%) as performances expected from materials in correspondence of these layers are limited and may be compared, in terms of stress, to the lower stresses of the fatigue testing carried out.

4. CONCLUSION

This paper discusses the possibility of employing plastics immiscible with bitumens (PVC and PET), derived from the differentiated collection of domestic wastes, in bituminous concrete mixtures for road pavements.

On the basis of the experience acquired from a previous experimentation, in which the best methods of employing were defined, five mixtures were studied, obtained by replacing in weight the equivalent granulometric fractions.

The purpose of this study was to carry out an investigation on the dynamic characterization of the mechanical properties and of the fatigue behaviour of the mixtures.

Mechanical properties were evaluated by determining the complex modulus E*. The results obatined suggested that the use of high RDP % renders bituminous concretes shorter to low temperatures and more ductil to high temperatures. Moreover, it was found that the viscous component of mixes tends to increase as RDP % increases; this aspect is even more marked in correspondence with low values of stiffness.

Fatigue strength of different mixtures was determined by submitting the specimens to repeated indirect tensile stresses by applying an impulse type of load, according to the controlled stress method. The values produced by testing allowed to draw the fatigue lines.

As it may be expected, the analysis of the results suggested that, as the plastics used increase, the fatigue strength of bituminous concretes decreases. However, it also came out that, in correspondence with the low value of the assigned stress, fatigue strength found may be compared to that of operating life required for road pavements.

To sum up, the mixtures analyzed provide satisfactory performances to be used in binder and base courses, if an adequate percentage of RDP is employed.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Leaching Standard For Quality Control Of Aggregates

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There are quite different attempts to investigate the environmental compatibility of materials which are regarded as wastes and which have to be disposed of on one hand and materials which are considered to be products on the other hand. For the assessment of the environmental compatibility of waste materials which are usually heterogeneous materials with variable composition and unknown origin extensive investigations (consisting of long term characterization, compliance and on site verification tests) are necessary.

For materials which are well known and have been used successfully for many years in building and civil engineering works - like aggregates - such extensive investigations concerning the environmental compatibility are not necessary. These materials have generally been submitted to detailed suitability tests in the laboratory and under practical conditions before putting them into use. Long-term experience has shown that these materials perform in an environmentally sound way.

To ensure that these materials comply with their certified or declared characteristics, production control is used. The production control system is based on continuous testing through factory production control and additionally by regular third party control. Since the production, processing and sale of aggregates is a continuous process, the tests used for production control should be simple and quick to produce results as promptly as possible. Furthermore the tests should produce results which have good reproducibility. Only in this way it is possible to reach quick and reliable pass/fail decisions.

A tank leaching test that was developed in Germany fulfils all these requirements and is therefore suitable for production control of aggregates. Since then this test has been adopted by CEN/TC 154 "Aggregates" in the European draft Standard.

1. INTRODUCTION

For some years European standardization committees have been concerned with the development of methods for the assessment of the environmental compatibility of materials. There are quite different attempts to investigate materials which are regarded as wastes and which have to be disposed off on one hand and materials which are considered being products on the other hand. For the assessment of the environmental compatibility of waste materials extensive investigations are necessary. According to the "Council Directive on the Landfill of Waste" [1] the general characterization and testing of wastes must be based on a three-level hierarchy consisting of basic characterization, compliance testing and on-site verification. The "Methodology for the determination of the leaching behaviour of waste under specified conditions" [2] gives suggestions on how to proceed with the investigation of unknown wastes taking into account waste-specific properties and scenario conditions. Such extensive investigations are justified because wastes are usually heterogeneous materials with variable compositions and unknown origin.

For aggregates that have been used successfully in building and civil engineering works for many years recurrent extensive investigations concerning the environmental compatibility are not necessary because these materials are well known. Such materials have generally been submitted to detailed suitability tests in the laboratory and under practical conditions before putting them into use. From these tests much information is available on technical properties and environmental behaviour. This information has been the basis for the setting of general requirements and specific limiting values for material properties. Long-term experience has shown that these materials perform in an environmentally sound way.

To ensure that a material complies with its certified or declared characteristics, production control is used. The production control system is based on continuous testing through factory production control and additionally by regular third party control. Since the production, processing and sale of aggregates is a continuous process, the tests used for production control should be simple and quick to produce results as promptly as possible. Furthermore the tests should produce results which have good reproducibility. Only in this way it is possible to reach quick and reliable pass/fail decisions.

The environmental compatibility of an aggregate is usually assessed on the basis of its leachability. It is known that leaching processes are very complex, depending on a number of different physical and chemical interactions. Laboratory tests cannot simulate all possible practical conditions in a satisfactory way. Therefore it is necessary to make simplifications in order to develop a quick and simple leaching test. A tank leaching test that was developed in Germany [3] [4] fulfils all these requirements and is therefore suitable for production control of aggregates.

2. HISTORY OF SHORT TERM LEACHING PROCEDURES

The DEV-S4 procedure (DIN 38414, Part 4 [5]) is currently the only leaching technique to be covered by a standard in Germany. It was the basis for the current German legislation, e.g. the Technical Instructions on Waste [6] and the Technical Instructions on Waste from Human Settlement [7]. In conformity with this standard the original structure of the material to be investigated should remain intact to the greatest possible extent. Normally only coarse pieces > 10 mm are crushed down, but in no case shall the sample be pulverised. 100 g of the material are put into a 2 l wide-necked bottle and are tumbled end over end with 10 times its weight of demineralised water for 24 hours. During the test the material shall be continuously in motion but additional crushing should be avoided.

This German test has now been include in the draft European Standard. Working group 2 of CEN/TC 292 "characterization of waste" has developed a draft standard for compliance tests for leaching of granular waste materials and sludges [8]. This draft standard includes four parts, differing from each other by different liquid/solid ratios (L/S) and/or different grain sizes. The first three parts require the material under investigation to be crushed to a grain size < 4 mm. Part 4 with L/S = 10 and a maximum grain size of 10 mm is more or less consistent with the German DEV-S4 procedure. There are only small differences between the European prestandard and the German standard, e.g. the dimension of the bottle should be selected such that the headspace is minimized.

Both pre-test processing and the continuous motion of the material during the procedure can serve to produce results with better reproducibility. Therefore these measures can be justified for the investigation of heterogeneous materials like wastes with variable compositions and unknown origin.

On the other hand such measures will lead to a change from the original structure of the material. As a result of the motion of the material throughout the leaching procedure some abrasion can occur which increases the leachable surface of the particles. Furthermore particular measures aiming at an alteration of the outer surface of the particles e.g. by weathering will be nullified by the mechanical action. Consequently the leaching rates will increase. Therefore abrasion should be avoided if well-known or pretreated aggregates are investigated.

The DEV-S4 procedure was originally developed for the investigation of materials with a very fine particle size like sludges and sediments, and for such materials it is still as suitable as ever. But for the reasons mentioned above this technique only has limited suitability for the investigation of road construction materials which generally consist of larger lumps.

For this reason it was seen as necessary to modify the DEV-S4-test. The working document No. 28/1 of the Forschungsgesellschaft für Strassen- und Verkehrswesen (FGSV, [9]) prescribes a modified DEV-S4 technique as a leaching procedure. This working document accordingly sets out a number of modifications in relation to the standardized DEV-S4 procedure; these modifications relate essentially to the grain size and quantity of the material to be investigated. The aggregates which are to be studied should be leached in quantities up to 2500 g in their original grain size. This modified DEV-S4 procedure is now more suitable for the investigation of coarse grained materials compared with the original standard but it still has some disadvantages. The greatest disadvantage is the abrasion which can occur by the motion of the material during the procedure. The larger the particles of the material to be investigated, the greater this effect will be.

Therefore the tank test was developed by the FGSV [9] which is even more suitable for the investigation of coarse grained materials. The advantage of the tank test, as compared with the modified DEV-S4 procedure, lies in the fact that it is unnecessary to agitate the entire container. Only the leaching medium is constantly circulated round the aggregate to permit intensive leaching within a short period of investigation. This avoids severe mechanical stress on the material undergoing investigation in the tank. The tank test fulfils all demands which are made upon a leaching test suitable for production control. The tank test has now been adopted by CEN/TC 154 "Aggregates" for the draft European Standard.

3. DEVELOPMENT OF THE TANK TEST

3.1 Selection of the leaching tank

Initially a rectangular tank, made of glass or polypropylene, was chosen with external dimensions of approximately 400 mm in height, a width of 250 mm and a length of 300 mm. For the leaching of organic substances a glass tank should be used while for the analysis of inorganic substances a tank made of either glass or polypropylene may be used. However, practical experience revealed problems with the rectangular shape. The fine grained material which had fallen through the meshes of the screen support piled up in the corners of the tank and it was not clear whether this material could be percolated by the leachant in a satisfactory way. Therefore cylindrical tanks with an approximate height of 400 mm and a diameter of 310 mm were chosen to avoid this problem [4].

3.2 Positioning of the sample in the tank

The intention was to position the sample in the tank in such a way that a good flow rate could be ensured around it. Therefore the material was not put directly on the bottom of the tank. A screen support was designed made of glass or teflon or polypropylene (in cases where only inorganic substances are analysed) with a removable screen (Figure 1). This screen with a height of 50 mm and a mesh size of 2 mm should be made of teflon or a teflon-like material. The screen can have a circular or a square shape and should be a distance of approximately 20 mm from the wall of the tank and 50 mm from the bottom of the tank. The mesh size of 2 mm was chosen for the reason that most of the material should be prevented from falling through the screen. On the other hand the mesh size should not be too small because otherwise the best possible percolation of the material from all sides could not be ensured.

For lightweight aggregates (e.g. expanded clay) the screen support has to be closed by a cover.

Before putting the material to be leached on the screen the screen support with screen is dipped into the tank which has been filled with the leachant. Then the material is distributed slowly and uniformly over the screen so that it is moistened and as much air as possible is displaced from the sample.

3.3 Selection of the stirring device

To prevent the development of concentration gradients around the grains and to ensure intensive leaching of the aggregate within a short period of investigation the leaching medium should be constantly circulated. Originally a magnetic stirrer with electronic rotational speed adjustment was used which could be positioned centrally below the tank (Figure 2). An egg-shaped teflon-coated magnetic stirrer bar was positioned on the bottom of the tank and the magnetic stirrer was set to a rotational speed of about 500 rpm.

It later became apparent that this stirring device had some disadvantages. Since the screen has a mesh size of 2 mm some of the material with smaller grain sizes can fall through the apertures. On coming into contact with this material the stirrer bar may become displaced beyond the range of the field driving it.

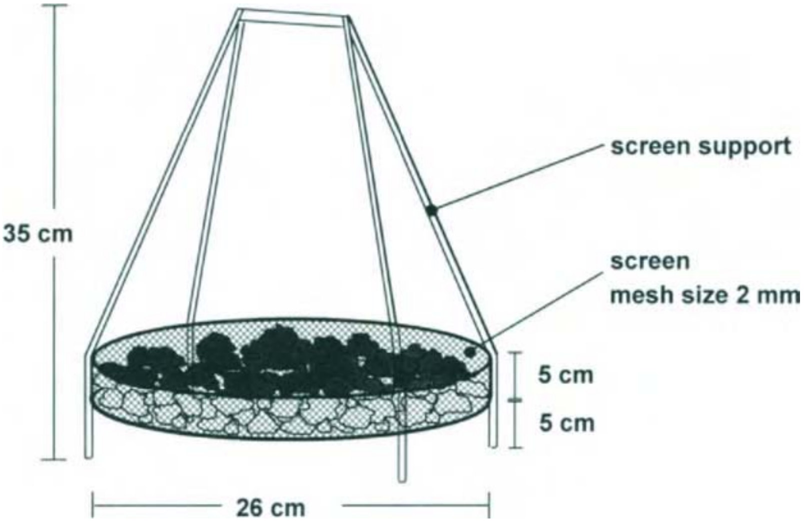


Figure 1. Screen support with screen

To prevent this a motor-driven dip stirrer was tested which is inserted through a small hole in the cover of the tank (Figure 3). The dip stirrer is fixed in such a way that it is close above the material. Good water circulation is assured with the stirrer in this position. The motor-driven dip stirrer is set to a rotational speed of 500 ± 20 rpm. Parallel leaching tests with both different stirring devices showed that the values are comparable.

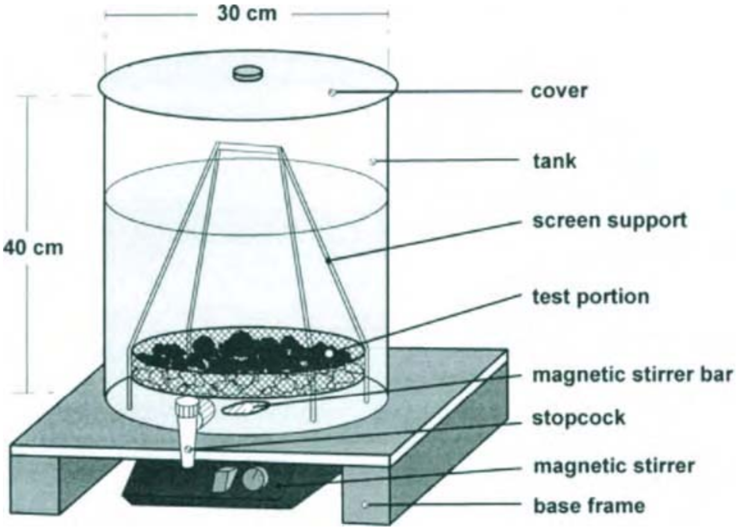


Figure 2. Tank leaching apparatus with magnetic stirrer

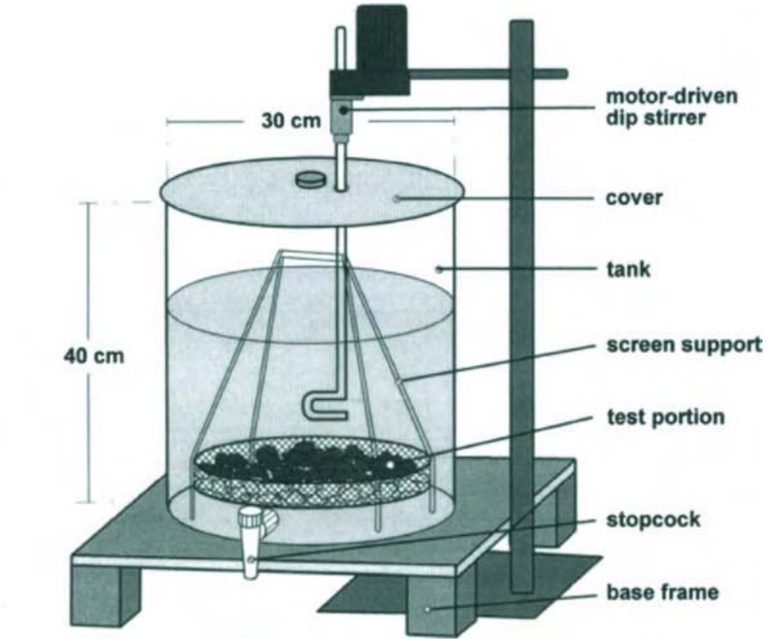


Figure 3. Tank leaching test according to prEN 1744-3

3.4 Selection of the leachant

The question arises as to what type of leachant should be used for the leaching standard. There are several possibilities as concerns the selection of the leachant: one can use demineralized water or artificial mineralized water. Experts have conflicting views on this question. For example the normalisation committee for drinking water (CEN/TC 164) recommends to take mineralized water of low hardness for the leaching of concrete. For the investigation of concrete which is exposed to flowing water, the use of artificial mineralized water may be most suitable. On the other hand a research study dealing with the "development of a leaching method for the determination of the environmental quality of concrete" has shown that there was no difference using synthetic water of low hardness compared with demineralized water. Sometimes it may be of advantage to simulate practical conditions as far as possible. In any case it is not possible to consider all occuring situations.

Therefore demineralized water was chosen as the leachant for use in the tank test. It is easy to prepare and widely available in laboratories. Demineralized water is a completely unbuffered system with a pH value of approximately 6 to 7. It will adopt the pH value of the leached material very quickly. This makes it suitable for the leaching of many different kinds of aggregates, including very basic or acidic materials. For example, when crushed concrete is leached with demineralized water using the test procedure, the pH value of the leachant exceeds 12 within less than one hour.

3.5 Duration of the procedure (reaching of near equilibrium)

A prerequisite for getting results with good reproducibility is reaching steady state conditions or near equilibrium during the test period. To check whether near equilibrium is reached, trials have been carried out considering a number of parameters with different materials.

pH value is one of the most important factors in the leachability of a material. Trials with air cooled blast furnace slag, electric arc furnace slag, recycled material and municipal waste incinerator bottom ash using the leaching procedure have shown that after 1 to 2 hours the pH value has already reached the approximate value of the "final" pH (after 72 hours). After 24 hours the pH value does not change very much. Similarly, the concentrations of other leachable compounds like heavy metals and salts change little after 24 hours.

Figure 4 shows some results from the trials. After 24 hours, more than 75 % and in most cases more than 85 % of the leachable components have been leached. This means that near equilibrium is reached. This applies to all three aggregate sizes used in the trials, 0/4, 0/10 and 0/32 mm, so coarse and fine-grained materials are all reaching near equilibrium.

3.6 Number of leaching steps

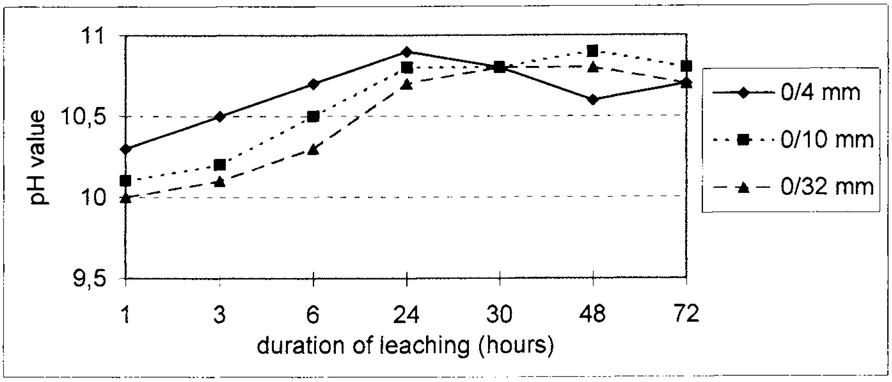
The most important mechanisms in the tank leaching test are the initial wash-off effect and the solubility of components from the outer surfaces of the aggregate particles. Diffusion processes, which are very slow, play only a minor role for the leaching of materials which are not bound, stabilized or monolithic. Therefore a single value obtained after 24 hours of leaching is sufficient to allow a decision to be made whether the material complies with the relevant requirements.

3.7 Sampling and sample preparation

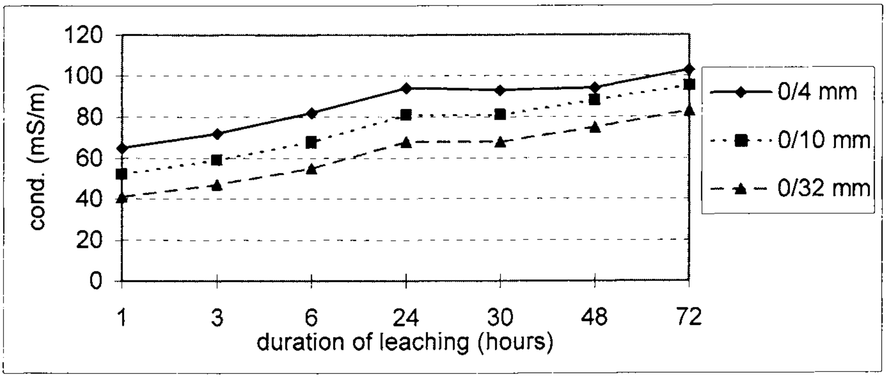
Sampling and sample preparation should be carried out in accordance with prEN 932-1 [10]. Aggregates with the particle size in which they are normally delivered shall be used. Fragments coarser than 32 mm should be crushed and the fraction 16/32 mm screened out. This is added to the 0/32 mm mixture to be analysed in the quantitative ratio in which the fraction > 32 mm was present in the original sample.

If the sample is wet it should be air dried at room temperature (< 40 °C) to constant mass before it can be divided and screened. The water content of the sample used for leaching is to be determined on a parallel sample by drying at 110°C in accordance with prEN 1097-5 [11].

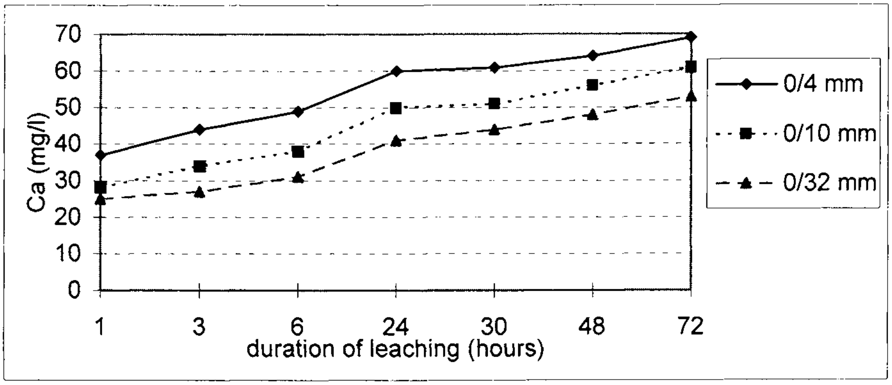
About 2 kg of sample material is weighed to the nearest 0.1 g for the leaching of unbound uncompacted materials in the tank.



Air cooled blast furnace slag

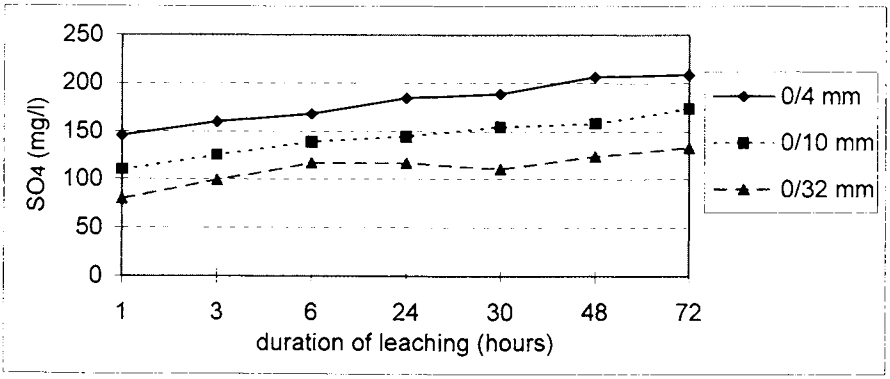


Electric arc furnace slag

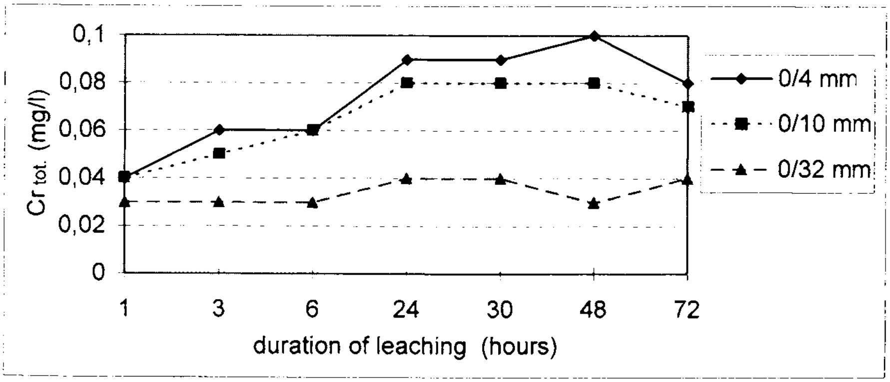


Recycled material

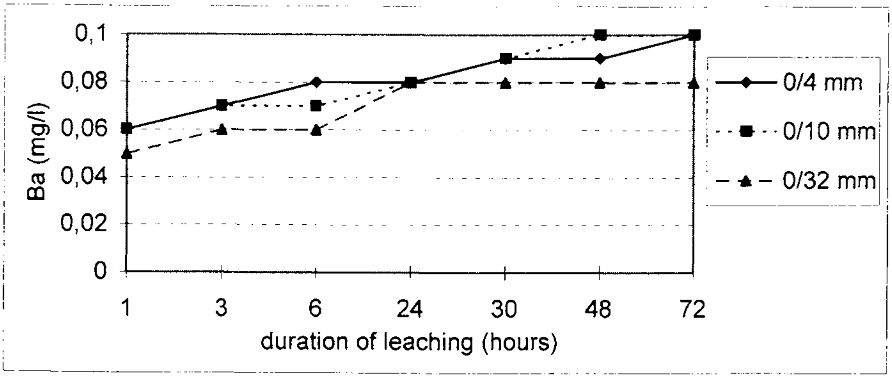
Figure 4a. Examples of the development of the leached concentrations with time (pH value, electrical conductivity, Calcium)



Air cooled blast furnace slag



Municipal waste incinerator bottom ash



Electric arc furnace slag

Figure 4b. Examples of the development of the leached concentrations with time (Sulfate, Chromium, Barium)

3.8 Leaching of organic substances

The tank test was originally developed for the leaching of inorganic constituents such as heavy metals and salts from aggregates. These constituents are the most important for the environmental compatibility of a great many aggregates. The leaching of organic constituents from aggregates is a subject that has not previously been considered in any depth. The processes that govern the leachability of organic compounds can differ considerably from those of inorganic compounds. Furthermore, sorption effects may play a more important role.

In many cases, the determination of organic parameters is required by legislation (e.g. for municipal waste incinerator ashes and recycled materials). Thus there is a need to examine the leachability of organic compounds. Unless a more suitable method is specifically developed, the tank leaching test should be used in the determination of organic parameters.

3.9 Reproducibility of results

The reproducibility of the results obtained from the tank leaching tests was investigated in the course of a research study [12]. Fifteen different industrial by-products and recycled materials were leached using the tank test and a range of inorganic and some organic parameters were analysed in the eluates. It could be seen that the reproducibility was very good for the inorganic parameters whereas it was not so good for the organic parameters especially for PAHs. However, the analysis of PAHs in aqueous media is difficult in general. That is the reason why PAHs are usually not analysed in eluates but in the solid material.

4. CONCLUSION

A clear distinction must be made between wastes which are usually heterogeneous materials with variable composition and unknown origin and aggregates which are well known and relatively homogeneous.

For waste materials extensive investigations concerning the environmental compatibility are significant and necessary. For aggregates which have been used successfully for many years a continuous production control is sufficient.

The environmental compatibility of aggregates is usually determined by reference to the concentrations of environmentally relevant components which may be leached out. Therefore a leaching standard is necessary for quality control of aggregates.

The described tank leaching test fulfils all requirements which are made of a test used for production control. It should be:

- Able to distinguish suitable material from material with inadequate quality
- Quick
- Simple in operation
- Able to give reproducible results
- Not too expensive

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Untersuchungen zur Übertragbarkeit von Grenz- und Richtwerten des Schüttelverfahrens nach DEV-S4 auf das Trogverfahren, July 1997

Waste Materials in Construction
G.R. Woolley, J.J.M. Goumans and P.J. Wainwright (Editors)

Products Of Steel Slags An Opportunity To Save Natural Resources

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1. INTRODUCTION

In Europe and the most other continents there is a great demand of aggregates mainly from civil engineering industry especially for the field of road and concrete constructions as well as for hydraulic purposes like stabilisation of river banks. But there are also the declared targets of the European Community [1].

- to protect the environment and to improve its quality,
- to serve the protection of the human health and
- to guarantee a cautious and efficient use of the natural resources.

The last statement of the declared targets holds us responsible to save natural resources by using industrial co-products and to increase their utilisation rate wherever their technical and environmental properties are suitable concerning the relevant application field.

Regarding the situation in Germany (see Figure 1) about 675 million tons of natural aggregates like gravel, sand and other processed rocks are produced and requested by the industry per year. Contrary to this balanced situation with natural aggregates the utilisation rate of about 174 million tons industrial co-products is much lower. Industrial co-products are e.g. slags and coal mining residues (81 million tons), recycling materials e.g. from demolition of concrete buildings (50 million tons) and other excavated materials from the building site (43 million tons). Their utilisation rate differs due to the technical and environmental properties of the relevant material between 10 and 100 %. In average it is only 48 %. Therefore, in Germany and in the other European countries the respective industry is concentrated on increasing the utilisation rate of industrial co-products and recycling materials [2] [3].

The steel industry has traditionally produced co-products which have been successfully used in many fields of application. A good example are the steel slags from Basic-Bessemer or Thomas process. Since 1880 these slags have been used as a phosphatic fertiliser. Since that time the steel industry investigated their slags continuously, took care of suitable processing and if necessary modified the iron and steelmaking processes to get slag products which fulfil the requirements of the specific standards and regulations. This work has mainly been done by Forschungsgemeinschaft Eisenhüttenschlacken (FEhS) – the German research institute for blast furnace and steel slags.

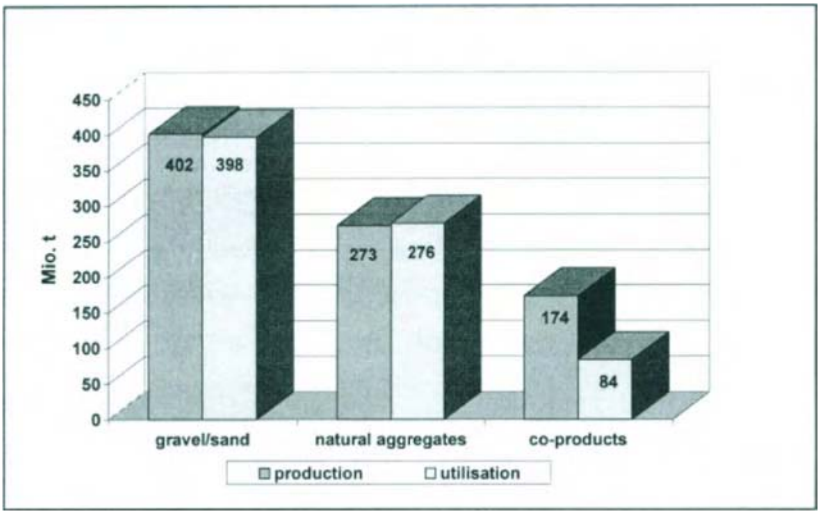

Figure 1. Production and utilisation of natural aggregates and industrial co-products

In Europe every year nearly 12 million tons of steel slags are produced. Owing to the intensive research work during the last 30 years today about 65 % of the produced steel slags are used on qualified fields of application. But the remaining 35 % of these slags are still dumped. It will need intensive further research work to decrease this rate as far as possible [4].

Contrary to the European figures the dumping rate of steel slags in Germany is 7 % only. So 93 % are used for different fields of application [3]. On the basis of the German experience with steel slags - these are Basic Oxygen Furnace Slags (BOF-slags) and Electric Arc Furnace Slags (EAF-slags) - this paper reports on the characteristics and properties of steel slags as an aggregate for road construction and hydraulic structure. In addition, the quality control system which has been established to consider technical and environmental aspects during the recent years will be explained.

2. GENERAL PROPERTIES OF STEEL SLAG AGGREGATES

2.1 Chemical and mineral composition

The BOF- and EAF-slags from different sources within Europe, as characterised by their chemical and mineral compositions plus their technical properties, are generally comparable and independent of their producers. Differences arise from the use of dolomite rather than lime with the effect of a higher MgO-content in the slag. Table 1 shows the range of the chemical composition of BOF- and EAF-slags.

BOF-slags and EAF-slags are calciumsilicatic with a range of CaO between 42 and 55 %, and a range of SiO_2 between 12 and 18 %. EAF-slags comprise CaO between 25 and 40 % and 12 to 17 % SiO_2. Their MgO-content may be higher due to the reactions with the refractory lining.

Table 1

Range of chemical composition of BOF- and EAF-slags (%)

Component	CaO	SiO_2	Al_2O_3	MgO	MnO	P_2O_5	Fe_{total}	CaO_{free}
BOF-slag low MgO-content	45 – 55	12 – 18	< 3	< 3	< 5	< 2	14 – 20	< 10
BOF-slag high MgO-content	42 – 50	12 – 15	< 3	5 – 8	< 5	< 2	15 – 20	< 10
EAF-slag low MgO-content	30 – 40	12 – 17	4 – 7	4 – 8	< 6	< 1.5	18 – 28	< 3
EAF-slag high MgO-content	25 – 35	10 – 15	4 – 7	8 – 15	< 6	< 1.5	20 – 29	< 3

The main mineral phases of BOF- and EAF-slags are dicalciumsilicate, dicalciumferrite and wustite. Dicalciumsilicate is stabilised by the P_2O_5-content of the slag which prevents a disintegration of the slag known from other slags. The content of free lime and free MgO is the most important component for the utilisation of steel slags for civil engineering purposes with regard to their volume stability. In contact with water these mineral phases will react to hydroxides. Depending on the rate of free lime and/or free MgO this reaction causes a volume increase of the slag mostly combined with a disintegration of the slag pieces and a loss of strength. Therefore, the volume stability is a key criterion for using steel slags as a construction material.

2.2 Technical properties

Static and dynamic forces and the environmental strains like rain, heat, freeze and thaw require adequate long term behaviour under these conditions for all constructions which are built today. Therefore, the technical properties of processed aggregates which are used for these constructions are of fundamental importance. The most important properties are:

- bulk density
- shape
- resistance to fragmentation (resistance to impact and crushing)
- strength
- water absorption
- resistance to freezing and thawing
- volume stability
- resistance to abrasion and polishing

During the past 30 years FEhS has investigated these properties of both, processed steel slag aggregates and established natural aggregates. Table 2 shows the mean values of selected properties derived from BOF- and EAF-slags, in comparison to granite and flint gravel.

According to Table 2 steel slags can be processed to aggregates of high quality comparable with those of natural aggregates.

Table 2
Technical properties of processed BOF- and EAF-slags, in comparison with established natural aggregates

characteristics	BOF-slag	EAF-slag	granite	flint gravel
bulk density (g/cm^3)	3.3	3.5	2.5	2.6
shape - thin and elongated pieces (%)	< 10	< 10	< 10	< 10
impact value (%/wt)	22	18	12	21
crushing value (%/wt)	15	13	17	21
10 % fines (KN)	320	350	260	250
polishing (PSV)	58	61	48	45
water absorption (%/wt)	1.0	0.7	< 0.5	< 0.5
resistance to freeze-thaw (%/wt)	< 0.5	< 0.5	< 0.5	< 1
binder adhesion (%)	> 90	> 90	> 90	> 85

The high bulk density of steel slags > 3.2 g/cm^3 qualifies steel slags as a construction material for hydraulic engineering purposes. In Germany about 400.000 tons per year are used as aggregates for the stabilisation of river banks and river beds against erosion.

All other technical properties listed in Table 2 are comparable or even better than those of natural aggregates. In particular the high level of strength described by the impact- and crushing value and additionally the rough surface texture are predominant. Both properties together with a high Polished Stone Value (PSV) and a binder adhesion > 90 % qualify these slags as aggregates for high trafficked road layers especially for asphaltic surface layers. More than 25 years ago in Germany test roads were built using steel slags as an aggregate for unbound and bituminous bound mixtures The test results confirm these good properties to the present day. The asphaltic layers had been resistant to deformation, rutting and polishing over this long term period.

These good experiences encouraged the steel industry and road administration to start further research work. The aim was to investigate the suitability of steel slags for noise reducing asphaltic layers. These layers are mainly characterised by a very high void content of nearly 20 % by volume. Therefore, only aggregates with a high resistance to abrasion and polishing are required. In 1993 a new test road was built in order to vary the aggregates used for the production of the surface layer. The test road was divided into three sections. One section was built with 100 % LD-slag, one with aggregates as a mixture of 50 % LD-slag and 50 % diabase and the third one for comparison with 100 % diabase aggregates.

Figure 2 shows the development of the skid resistance measured on the top of the surface layer with the "Sideway Forced Coefficient Routine Investigation Machine - SCRIM" from 1993 to 1998. It is obvious that there is no decrease of the SCRIM-values since finishing the test road in 1993. On the contrary the SCRIM-values of all sections arise slowly. Section number 1 and section number 3 with LD-slag and diabase respectively show the same level of SCRIM-values. This means that there are no significant differences between the abrasion and polishing behaviour of LD-slag and diabase as a well proved natural aggregate.

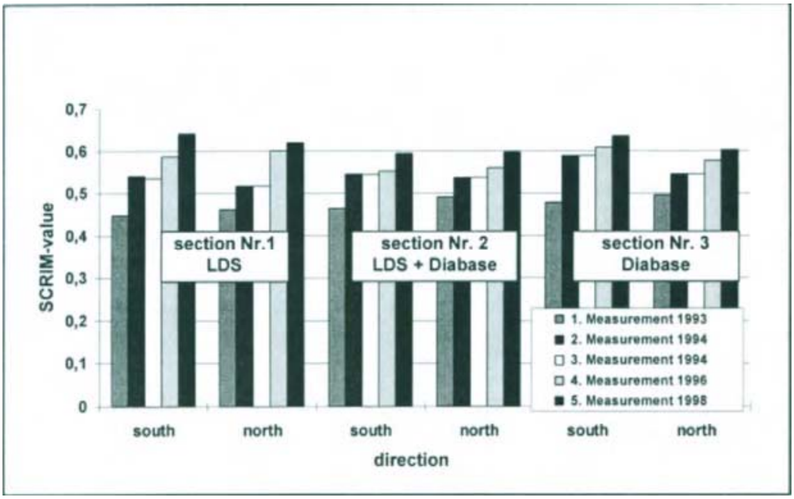

Figure 2. Development of SCRIM-values on asphaltic surface layer built with LD-slags

But all these pretentious applications of steel slags are only practicable if there is a sufficient volume stability as the decisive criterion.

To guarantee a sufficient volume stability the steel works employ different ways of slag treatment. The most applicable ones are the following:

- Determination of the free lime content by analysing samples from the liquid slag out of the converter and pouring slags of high or low free lime content into separate pits. To determine the free lime content the ethylene glycol method or statistical formulas on the basis of the mineralogical composition may be used. In Germany a limit of 4 % for the free lime content is mostly used as a separation criterion. But this method is only applicable if the steel making process works without the addition of dolomite lime and if steel slags are produced with low MgO respectively low free MgO contents.

- Weathering of the solid slags outside the slag pits for a certain period of time at free atmosphere to transform the free lime into calciumhydroxide. In some cases the slag is also sprayed with water to accelerate the hydration of free lime and/or MgO. But weathering takes time, needs a lot of storage space and produces fine grained slag which is hardly applicable as a construction material.

- Treatment of the liquid slag outside the steelmaking process in a separate slag pot, so that the steel quality will not be influenced by this slag treatment and the steelmaking process is not extended. Together with Thyssen Krupp Stahl AG the FEhS developed such a method by laboratory tests and tests in the steel shop [5]. The process works on the basis of the injection of oxygen and dry sand into the liquid slag. Thus additional heat is generated to keep the slag liquid and to dissolve the sand. The slag ratio CaO/SiO_2 is reduced and the free lime is dissolved and chemically bound. In 1996 the treatment equipment was installed in line of converter no. 1 of the steel shop of Thyssen Krupp Stahl

AG, Duisburg, since this time it works successfully. The free lime contents of all slags determined produced by this treatment show amounts less than 1 % by weight. Thus they do not show any volume increase. Free MgO will react in the same way as free lime.

The treatment of slag chosen in steel works generally depends on the requirements for the volume stability which are different depending on their application. For certain applications, no restrictions on the volume stability are necessary, e.g. unpaved roads, parking areas and dams. But if steel slags are used in unbound and bound layers of roads the volume stability must be within certain limits. The question arises how to measure the volume stability and which requirements have to be fulfilled.

For fresh and separated steel slags with a low MgO content which have not been weathered the free lime content determined by the Ethylene Glycol Method may be used as a criterion for the volume stability. In Germany experience has found that steel slags with a free lime content up to 7 % may be used in unbound layers and up to 4 % in asphaltic layers.

But for unclassified slags and slags with a higher MgO content this method does not work because the Ethylene Glycol Method does not differ between hydrated and unhydrated free lime. Furthermore, at present there is no reliable quick test method to determine the content of free MgO as a decisive criterion in the steel shop.

When using slags for road construction hydration develops mainly from the reaction between water vapour and free CaO and/or free MgO. Therefore, in Germany several test methods have been developed and tested to get information about the expansion capacity of steel slags. FEhS started these investigations in 1978 with autoclave tests, but, the test conditions – high temperature of 215 °C and high pressure of 21 bar – are extremely unrealistic. Additionally the investigations came to the conclusion that using autoclave conditions mineral reactions occur which have never been found in the field under natural conditions. After that water storing tests were carried out with the result that there appeared wash off effects of free lime and/or free MgO during water storage. Therefore, the tested samples very often simulated a satisfying volume stability which was not verified when other test conditions were chosen e.g. storage in a humidity chamber. This was the beginning of the development of the steam test.

The principle of the steam test is uncomplicated. As shown in Figure 3 a compacted slag specimen with a defined grain size distribution 0/22 mm is subjected to a flow of steam of about 100 °C in a steam unit at ambient pressure .By these means, the necessary moisture for the reaction of free lime and free MgO is continuously conveyed to the test sample.

The volume increase caused by this reaction is read off from a dial test indicator at the surface of the specimen. The increase in volume is given as the result, calculated in % by volume of the compacted slag specimen. From 1980 the steam test has been used in Germany as a method for the quality control for steel slags relating to the factory production control and the third party control. Today it is a routine test which during recent years has helped to avoid damages caused by unstable steel slag aggregates.

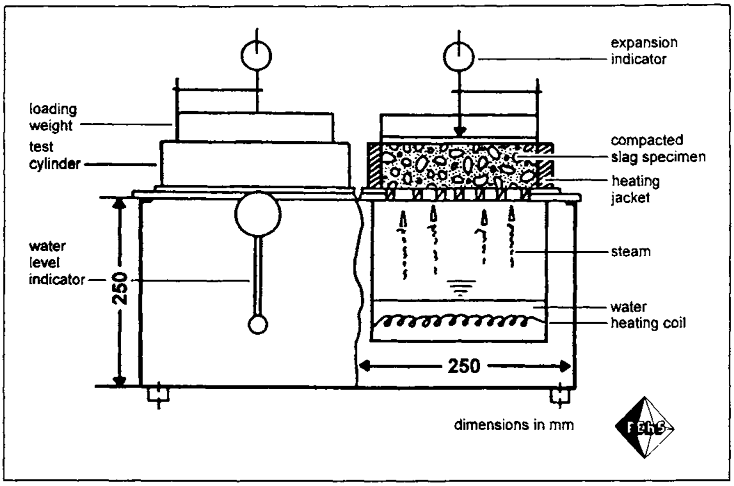

Figure 3. Principle of the steam test

Meanwhile the steam test is accepted by the European countries as a harmonized test method and has been incorporated into European aggregate standards as a test method for steel slags. It is part of EN 1744-1 "Tests for chemical properties of aggregates – chemical analysis" [6] which was published officially by CEN in 1998.

Figure 4 shows a typical test result achieved by using the steam test. It shows the development of the volume increase of a LD-slag in respect to time. The curve is typical for all steel slags. Initially the rate of the volume increase is high but decreases with time almost to zero. The slope of the curve depends on the slag type, mainly on the free lime and/or the free MgO content. The curve statistically can be calculated by a formula to predict the final volume increase. The tests which have been completed during the last 10 years have shown that for LD-slags with a low MgO content < 5 %, 24 hours testing time is sufficient because after that time the rate of the volume increase has nearly finished. LD-slags with a higher MgO content > 5 % and EAF-slags have to be tested for 168 hours because the hydration of MgO takes more time than that of free lime.

In the meantime the steam test method has been discussed on the European level by the responsible task group 8 of TC 154 "Aggregates". This task group tried to find suitable requirements as a suggestion for the product standards developed in the subcommittees 3 and 4 of TC 154. It took a long time to develop a harmonised version which considers the different experiences regarding steel slags, national specialities of treating slags, and the philosophy of road construction. The result of the discussions which was finally accepted by TC 154 is given in Table 3.

Different categories of requirements V_A to V_D have been developed due to the maximum expansion. These categories can be chosen by the European countries on the basis of their national experience with steel slags and their individual fields of application. The class V_D states that there is no necessity of testing the volume stability of slags if the national experience confirms a satisfactory performance record. The categories given in Table 3 are part of the aggregates standards drafted by TC 154 [7] [8].

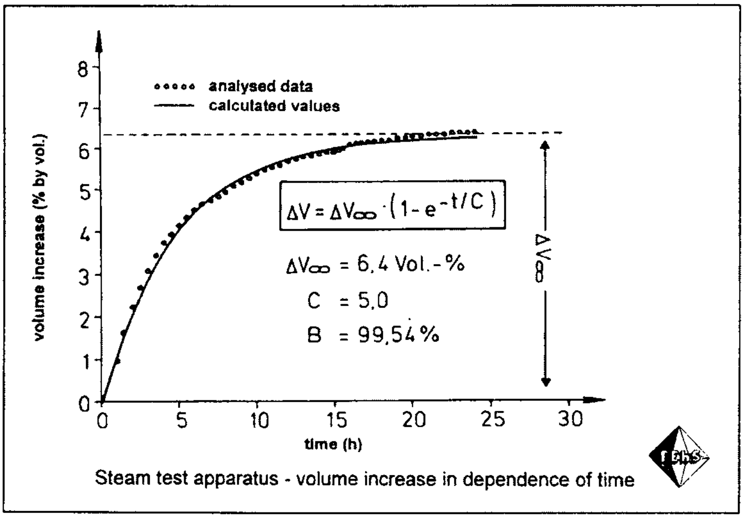

Figure 4. Typical volume increase of steel slags tested by the steam test

Table 3
Maximum expansion values for steel slag aggregates

type of steel slag	maximum expansion (% by volume)		testing time	category
	aggregates for bituminous bound mixtures	aggregates for unbound mixtures	(hours)	
BOF-slag/EAF-slag (MgO ≤ 5.0 %)	3.5	5	24	V_A
BOF-slag/EAF-slag (MgO > 5.0 %)	3.5	5	168	
BOF-slag/EAF-slag (MgO ≤ 5.0 %)	6.5	7.5	24	V_B
BOF-slag/EAF-slag (MgO > 5.0 %)	6.5	7.5	168	
BOF-slag/EAF-slag (MgO ≤ 5.0 %)	10	10	24	V_C
BOF-slag/EAF-slag (MgO > 5.0 %)	10	10	168	
BOF-slag/EAF-slag (MgO ≤ 5.0 %)	no requirement			V_D
BOF-slag/EAF-slag (MgO > 5.0 %)				

According to German experiences steel slag aggregates are suitable for unbound layers respectively for asphalt layers if the expansion does not exceed the requirements for category V_A. Steel slag aggregates, therefore, have a suitable volume stability if the expansion is limited to 5 % and 3,5 % respectively.

When slags are used for hydraulic structure purposes as armourstones free CaO and/or free MgO will react with water as a liquid. Therefore, a separate expansion test has been developed for this purpose by the Expert Group "Armourstone" of SC 4 of TC 154. The Expert Group developed the boiling test on the basis of a similar test method which is used in the Netherlands for many years. Using this test method 20 slag pieces with a diameter of 50 to

150 mm have to be placed in a bath of boiling water and shall be left there over a time of 8 hours. After this time the loss of mass of the slag pieces has to be determined.

Just as for steel slag aggregates for road construction the Expert Group "Armourstones" had to establish suitable requirements for armourstones too. Again it took a long time to come to harmonised requirements because there were different experiences to calculate and to interpret the test results. As a result the Expert Group established two categories due to the loss of mass after finishing the boiling test as it is given in the following:

Category A:	Maximum 4 of the 20 test pieces are allowed to show more than 0,5 % loss of mass
Category B:	The total loss of mass of all test pieces shall not exceed 5 %

The boiling test method is described in draft prEN 13383-2 Armourstone – Test methods [9] and the requirements in draft prEN 13383-1 Armourstone – Specifications [10]. Both drafts have been presented to the European countries in order to ask for comments in 1999.

2.3 Environmental behaviour

When industrial co-products are used as an aggregate water resource implications must be taken into account particulary from the durability aspect. Basically the assessment of the environmental compatibility of aggregates as a building material is not determined by the content of environmentally relevant elements in the solid material but by the potential leaching behaviour. Therefore, the major element analysis and the mineral composition as given by Table 1 are essential but not sufficient for an evaluation of environmental impact. To get information about the effect on the ground water and soil it is of more interest to know the concentrations of those environmentally relevant components which can be leached out. To simulate the leaching of aggregates in laboratory during the past 10 years in Germany and other European countries many leaching tests methods have been developed. Watching the developing work especially that of TC 292 "Wastes" it has to be pointed out that aggregates that are well known and have been used in the long term and which are continously quality controlled need not to be tested by so-called characterisation tests. It is sufficient to control their leaching behaviour continuously by a short term compliance test.

At present the only leaching technique which is standardised in Germany is the DEV-S4 method described in DIN 38 414 [11]. This technique works with a constant overhead rotation and places mechanical stress on the material so that new fracture surfaces and varying degrees of abrasion are liable to occur. Therefore, this method is unsuitable for describing the leaching characteristic of aggregates and so a new leaching test technique was developed on the basis of existing tank methods. This leaching method is given in Figure 5. It differs from the DEV-S4 method essentially in that the leaching sample is not moved, only the water. This has the advantage that additional strain on the investigated material is avoided. Furthermore this technique also enables larger (hardened) test samples to undergo leaching. This technique has been sufficiently tested during the last 5 years as a routine investigation procedure. Therefore, it was suggested as an European test method for leaching aggregates. In the meantime the tank leaching test was harmonised and drafted by task group 8 of TC 154 as part 3 of the EN 1744 [12]. The draft of EN 1744-3 will be presented to the European countries as CEN-Enquiry at the end of 1999.

In Germany the tank leaching test is officially used as a controlling method for factory production and third party control when slags are applied as aggregates for road construction and hydraulic structures.

The leaching test results have shown, that except for the pH value, which is affected by the partial solution of the slag lime, and the closely-related electric conductivity, the leaching of other elements is insignificant in terms of environmental impact. Chromium as mineral component may occur in somewhat higher amounts. But the concentrations in leachates are low because the chromium ions are bound within stable crystalline phases. All other concentrations of heavy elements are very low and not relevant under environmental aspects. Organic substances do not exist in slags because of the high melting temperature of about 1600 °C.

In Germany steel slags processed to aggregates for road construction and hydraulic structures have to be analysed by leaching tests two times per year. The concentrations of the leachate have to fulfil the requirements of relevant parameters listed in Table 4. If the requirements given in Table 4 are met, then steel slag aggregates are applicable for all uses in road constructions and hydraulic structures.

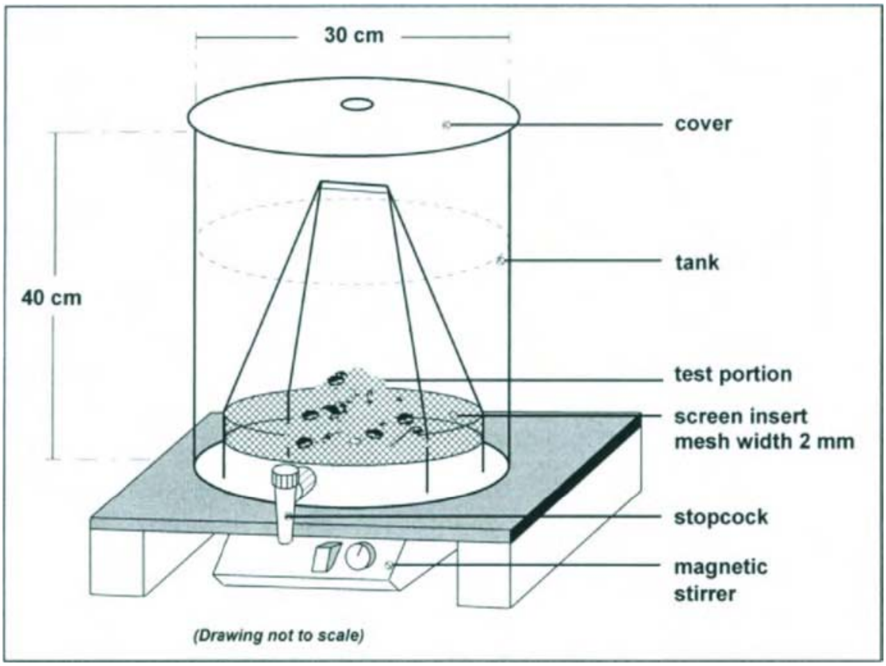

Figure 5. Tank leaching test apparatus

Table 4
German requirements for concentrations of leachates using steel slag aggregates

parameter	steel slag		
	road construction	Hydraulic structure	
relevant aggregate size	all in	< 60 mm	> 60 mm
pH-value	10 – 13	11	10
Electric conductivity (mS/m)	500	80	60
chromium (mg/l)	0.03	0.03	0.03

3. QUALITY CONTROL AS A BASIS FOR A SUCCESSFUL APPLICATION

In order to ensure a permanent satisfying quality control of all slag products which are used for the building site the German slag producers and processors control their products continuously by a factory production control. The performance and the results are certified regularly by a third party control institute twice a year. This controlling system was established by the German association for quality control of metallurgical slags – Gütegemeinschaft Eisenhüttenschlacken e.V. (GGEHS) – together with the German road and waterway administration 30 years ago. The production control requirements were adapted continuously to the latest development in quality control systems. The factory production control includes the

- production management,
- process control,
- inspection, calibration and testing of the equipment,
- inspection and testing of the produced slag products,
- handling and delivery.

The third party control institute evaluates the factory production control and controls the products twice a year by a separate investigation concerning all relevant technical and environmental properties like volume stability and leaching behaviour. As an example for road construction products Table 5 gives a summary of the general properties and suitable test methods performed regularly by factory production control and third party control.

If all elements of the factory production control system and those of the third party control conform with the requirements the producer will be certified by the GGEHS. After that he is permitted to mark his delivery tickets with the emblem of the GGEHS (see Figure 6) as a sign of a successful certification.

Table 5
Quality control of steel slag properties – test frequencies

	Property	Test frequency		Test method
		Factory production control	Third party control	
1	Petrografic characteristics		1 per 2 years	DIN EN 932-2/3
2	particle density	1 per week	2 per year	prEN 1097-6
3	Particle size distribution	1 per week	2 per year	prEN 933-10
4	Particle shape	1 per week	2 per year	DIN EN 933-3/4
5	Organic matter	1 per day	2 per year	DIN EN 1744-1
6	Resistance to fragmentation		2 per year	DIN EN 1097-2
7	Resistance to freeze-thaw		1 per 2 years	DIN 52104
8	Water absorption	1 per week	1 per 2 years	prEN 1097-6
9	Volume stability	1 per week	2 per year	DIN EN 1744-1
10	Resistance to polishing		1 per 2 years	prEN 1097-8
11	Leaching properties	2 per year	2 per year	prEN 1744-3

Figure 6. Emblem of the Gütegemeinschaft Eisenhüttenschlacken e.V.

4. SUMMARISED EXPERIENCES WITH THE APPLICATION OF STEEL SLAGS

Steel slags have been produced and used successfully in different European countries as a *road construction material* because of their advantageous technical properties. In order to confirm these practical experiences test roads have been built more than 25 years ago in agreement with steel producers and the road building administration. Thus steel slags were used not only for unbound layers like road bases and sub bases but also for bituminous bound layers like surface layers. All test roads have been built according to the German standards concerning aggregates and dimensioning urban roads and highways. Furthermore all test roads have been divided into several sections which gave the possibility to investigate steel slags in comparison to experienced natural aggregates like crushed gravel or artificial aggregates like blast furnace slag.

By building test roads the following results could be achieved:

- The crushed and rough surface of processed steel slag aggregate mixtures effects a strong bearing capacity directly after compaction higher than using other aggregates.
- There is no influence of heavy rain on the bearing capacity of unbound layers build with steel slag mixtures.
- The carbonatic solidification leads to an increase of bearing capacity.
- The aggregate mixtures are permanently stable if the requirements for the volume stability have been fulfilled.
- The asphaltic surface layers remain permanently plain even under heavy traffic.
- The resistance to polishing of asphaltic surface layers remain of a high level over a long term period.
- Roads built with steel slags as an unbound or bituminous bound aggregate do not influence the environment by leaching.

In the field of *hydraulic structures* steel slags are mostly used for

- dams and dikes
- stabilisation of river bottoms
- refilling of erosion areas on river bottoms
- stabilisation of river banks

Usually aggregate sizes > 10 mm are used to prevent a wash off effect of fine particles. Mainly the high density, the high level of strength and abrasion as well as the rough texture of processed steel slag aggregates ensure a long term resistance to dynamic forces coming from waves and river flow.

The long term behaviour of hydraulic constructions made by steel slags has been investigated by FEhS together with German river authorities regarding

- the volume stability
- the effects of leaching
- the effects on the river fauna

Summarised the results show that the properties of steel slag armourstones are comparable to those of experienced natural stones like basalt.

The engineering and ecological properties of steel slags are accepted in many countries and are widely used as a construction material. In Germany the fields of road- and waterway construction have made a very significant contribution to the present utilisation rate of about 93 %. Thus the use of steel slags saves existing resources of natural aggregates.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Accelerated ASR testing of recycled concrete

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The work involves research on investigating techniques and procedures to assess the Alkali Silica Reactivity (ASR) expansion potential for concrete made from recycled concrete aggregate (RCA) which was known to have ASR, or is capable of ASR under conditions of increased alkali. Laboratory testing was done to evaluate various testing procedures designed to accelerate the ASR reaction. This included evaluating prisms with variable surface to volume ratios, increased moisture state, and microwave energy.

Standard 280 mm prisms with 76.2 mm faces cast with four 6.35 mm parallel longitudinal holes were shown to not only accelerate ASR but also to lower the coefficient of variation of the expansion data. Expansion of 76.2 mm concrete cubes was found to be significantly accelerated as compared to that of a standard prism. Sealing prisms in evacuated plastic bags with water was also found to effectively accelerate ASR expansion. Concrete prisms were subjected to ASTM C 1260 and ASTM C 1293 conditions and the results were compared to those from modified versions of the same tests including the use of microwaves.

1. BACKGROUND

The United States highway infrastructure consists of a significant amount of concrete pavement. Some of the pavements are known to have Alkali-Silica Reaction (ASR), as suggested by the work conducted during the Strategic Highway Research Program (SHRP), and will eventually require rehabilitation, replacement or recycling. Recycling Portland cement concrete pavement has been shown to be a viable alternative to replacement or overlaying (*1*). It is very difficult to evaluate existing concrete for use as Recycled Concrete Aggregate (RCA) when the concrete being considered has shown ASR deterioration. Such concrete must be given extra consideration prior to use as RCA (*2*).

Current practice for evaluating the potential effect of an aggregate to be utilized in a proposed concrete is time consuming and is limited to testing of mortar and concrete prisms. A need exists for a new ASR evaluation test that could be conducted on the actual concrete mix proposed using either new aggregate or RCA. One major problem in the development of such a test is that substantial reaction must occur before it is measurable as an expansion. In that ASR requires time to develop, it is essential the new test be accelerated so test results are made available in a timely manner.

A highly recognized prescreening aggregate test, presently used in the US, is the ASTM C 1260 test (*3*). This test works well when used as a screening test to evaluate an aggregate for potential ASR. The proposed aggregate is ground to a specified grading and small 25 mm in cross-section and 280 mm long mortar bar prisms are cast. Neither test is recommended for use other than as a screening test for determining potentially reactive aggregate because they have not been correlated to actual field performance. Mortar bars are monitored for expansion while submerged in 1 normal NaOH solution at 80 °C for 14 days. A RCA cannot be evaluated using these tests as is because the test requires the aggregate to be reduced in size to make the mortar bar specimens. The results of such testing would at best confirm what is already known i.e. that the original aggregate is in fact susceptible to ASR.

A test commonly used for evaluating aggregate for ASR expansion in a concrete mix is the ASTM C 1293 test (*4*). Although highly accepted as a viable test, the major disadvantage of this test is that it must be monitored for up to one year. A faster test is certainly needed.

David Stark at CTL (*5*) and more recently Benoit Fournier at the International Centre for Sustainable Development of Cement and Concrete (*6*) have subjected concrete prisms to conditions similar to those in the ASTM C 1260 test. Although the results of Stark (*5*) were not as encouraging as those of Fournier (*6*) there appears to be a good correlation between field performance and the expansions obtained from the testing of the large concrete samples. Fournier (*6*) has developed expansion criteria based on correlations with field performance. These criteria show a good correlation between 0.04% expansion at one year for samples held at 38 °C and >95 % RH (similar to ASTM C 1293) and with samples held at 80 °C in 1 normal NaOH for 4 months (modified ASTM C 1260) and with samples held at 38 °C in 1 normal NaOH for six months. These criteria have not been evaluated for RCA concrete. Other ways of accelerating ASR have been evaluated such as steam curing (*7*), but none have been shown to be time effective.

The use of RCA in concrete compounds the problem of testing for potential ASR because of the uniqueness of a given RCA. For instance, an RCA obtained from a pavement made with reactive aggregate and low available alkali cement could become very reactive when used in new concrete with high available alkali. On the other hand, if the available alkali has been converted to alkali silica gel the reaction in a RCA would not be problematic providing the available alkali was restricted in the new concrete mix. Testing of RCA using existing testing procedures like ASTM C 1260 would be expected to show it to be very problematic whereas in reality it may not be, depending on the properties of the cement utilized.

This paper presents the initial findings of the development of accelerated testing procedures to evaluate concrete made with RCA, which has either undergone ASR or potentially could develop ASR under increased levels of alkali.

2. MATERIALS

A section of Wyoming I-80 near Cheyenne originally placed in 1965 and consisting of a 200 mm thick Portland cement concrete pavement was recycled during the Fall of 1985 and Spring of 1986. The original pavement was found to have ASR and, to prevent it from reoccurring in the recycled mix, a low alkali (< 0.60 %) Type II Portland cement and class F fly ash were specified, and the RCA coarse aggregate was "sweetened" with crushed limestone. Mix proportions and properties of the recycled mix are presented in Table 1. Some sections of the new recycled pavement have begun to show ASR several years after being placed.

The aggregate used in the I-80 concrete was selected as a test aggregate to develop accelerated ASR tests. Geologically this aggregate is of volcanic origin (granite, basalt, diorite, crystal-vitric tuff, rhyolite, and andesite) and contains a variety of minerals. The Portland cement elected as a laboratory control (except as noted) had an equivalent Na_2O alkali content of 1.37% (K_2O = 1.45% and Na_2O = 0.42%) with a MgO content of 3.2% and an autoclave expansion of 0.11 %. A quantity of the original reacted section of I-80 was obtained and purged with nitrogen to prevent carbonation until crushed and used as an RCA in the test mixes.

The concrete test mixes as shown in Table 1 were proportioned with 402.7 kg/m^3 of cement, 1,151.6 kg/m^3 of coarse aggregate and 827.9 kg/m^3 of fine aggregate with a water-cement ratio of 0.43 and an air content of 6% +/- 1%. The coarse aggregate was either the original Wyoming aggregate or the RCA from I-80 without fines and is referred to as WY aggregate or WY RCA respectively. The fine aggregate was a local innocuous glacial sand.

Table 1
I-80 Recycled concrete and test concrete mix design and properties

Component	I-80 Recycled mix, kg/m^3	Laboratory test mix, kg/m^3
Cement	290	402.7
Fly ash	79	None
Coarse aggregate RCA	657	1152
Coarse aggregate new	357	None
Fine aggregate RCA	150	None
Fine aggregate new	523	828
Water reducer and air Entrainment	As recommended by manufacturer	As recommended by manufacturer

Property	I-80 Recycled mix	Laboratory test mix
Air	4 to 7 %	6 +/- 1%
Slump	12 mm to 50 mm	As obtained with fixed w/c
W/C	< 0.47 target = 0.44	0.42
Flexural strength	5.2 MPa in 28 days	Not specified

3. PROCEDURES

The basic testing procedures of ASTM C 1260 and ASTM C 1293 were used as the fundamental starting point to evaluate new methods in an effort to develop a new test procedure with increased rate of expansion which would be applicable for use with conventional as well as RCA concrete. The preferred test would not increase the alkali content past the level expected under actual field conditions and of course must be accelerated so a quick decision on mitigation may be made and evaluated prior to specifying the final concrete mix.

The variables that were selected for evaluation included the surface to volume ratio of the test samples, moisture state, and the probability of an OH^{-1} ion coming in contact with reactive silica in the aggregate.

The surface to volume ratio was selected as a variable based on the premise that reaction rate should be increased by varying the effect of diffusion of moisture and alkali into the sample. The different shapes and their surface to volume ratios evaluated are presented in Table 2. The standard smaller 25 mm x 25 mm x 280 mm molds used in the ASTM C 1260 were replaced with larger 76.2 mm x 76.2 mm x 279 mm molds, some with four parallel holes as shown by Figure 1. The holes were spaced such that a 19 mm maximum aggregate size could pass between them during casting of the prisms. Surgical tubing was used to form the holes by stretching it over steel rods within the steel molds. Figure 2 shows the smaller 75 mm cube samples that were cut from the standard prisms.

Moisture state was varied on some samples by wrapping the samples with Saran® wrap, duct taping both ends, and vacuum sealing in a bag with 25mm of water. Microwave energy was evaluated as a potential reaction rate accelerator.

Table 2
Test sample shapes evaluated

Shape	Surface/volume
76.2 mm x 76.2 mm x 279 mm solid prism	0.589 cm^{-1}
76.2 mm x 76.2 mm x 279 mm prism with four 6.35 mm holes	0.611 cm^{-1}
76.2 mm x 76.2 mm x 76.2 mm solid cube cut from a large solid prism	0.787 cm^{-1}
76.2 mm x 76.2 mm x 76.2 mm cube cut from a large prism with holes	0.808 cm^{-1}
50.8 mm x 50.8 mm x 279 mm cut from the standard solid prisms	0.860 cm^{-1}

3.1. Modified ASTM C 1260

ASTM C 1260 was modified such that concrete samples could be evaluated. Modifications, other than the larger size samples, included using a smaller volume of alkali solution and not adjusting the mix alkali to 1.25%. A 0.75 volume of 1 normal NaOH solution to unit volume of test sample was selected so as to conform to earlier work done by Benoit Fournier at the International Centre for Sustainable Development of Cement and Concrete (*6*). Maintaining the larger ratio as specified in the standard test is not practical due to the large tanks required.

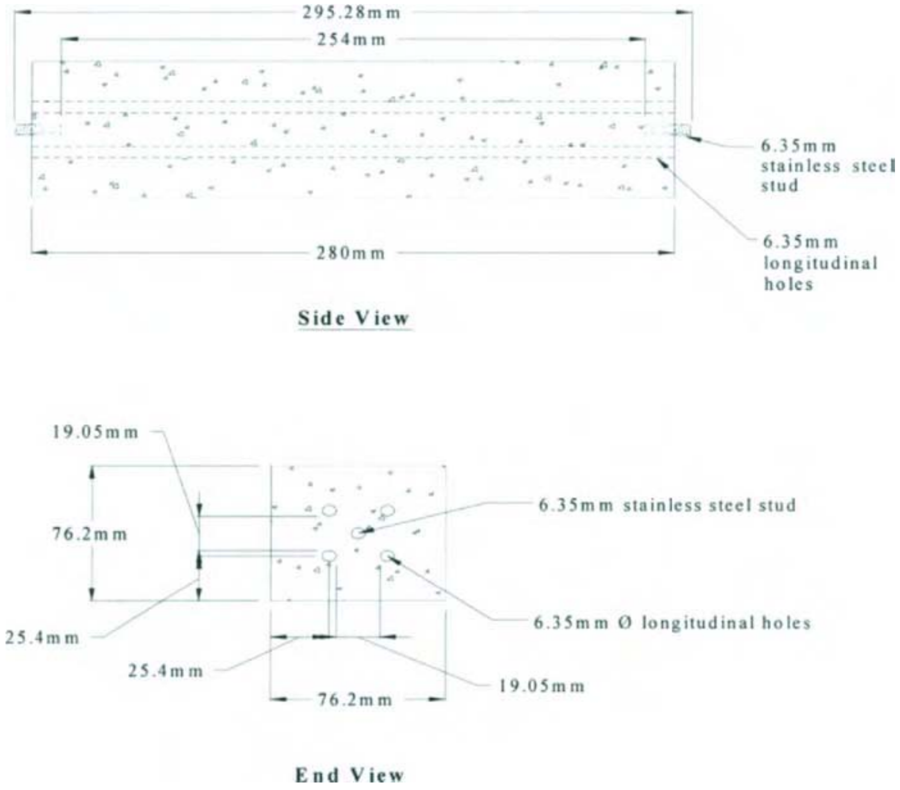

Figure 1. Side and end view of the prisms with cast longitudinal holes.

3.2. ASTM C 1293 Test

This test was used as a comparison for the accelerated expansions of the evaluated tests. The object was to have statistically significant expansions comparable to the one year ASTM C 1293 but in a much shorter time period.

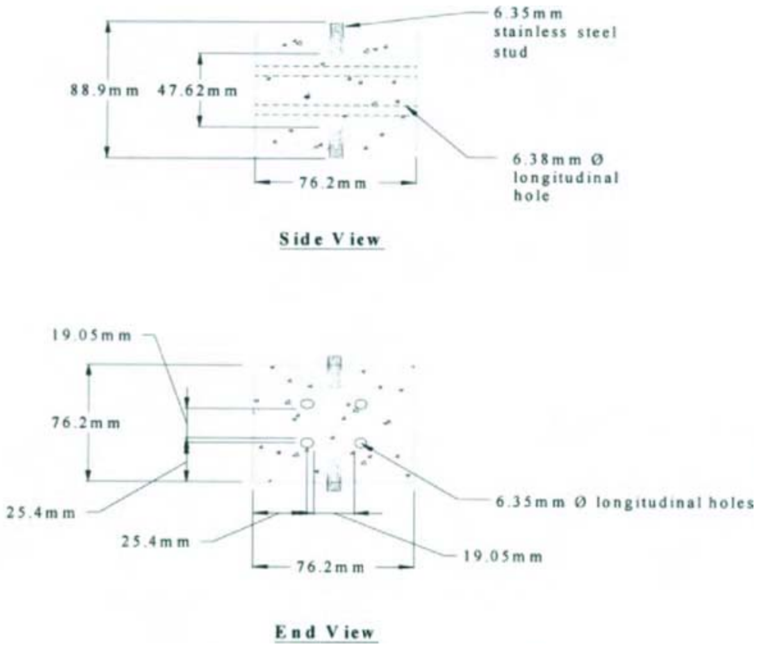

Figure 2. Side and end view of the cubes cut from the large prisms with cast holes.

3.3. Microwave Energy

Microwave energy has been used in the concrete industry to determine the water-cement ratio of plastic concrete (*8*), and to accelerate the curing of concrete (*9*). The microwave test was mechanically set up such that air at 38°C was discharged from the ASTM C 1293 test into a large insulated box, which contains six microwave ovens. Each oven has a high temperature safety shut off circuit and a timer to turn the magnetron on and off to control the amount of energy dispersed to the concrete. The procedure was to hold the samples at 38°C while applying repeating bursts of microwave energy (7 seconds every 10 minutes giving a total of about 16 minutes of 1100 watts of microwave energy per 14.79 kg of sample per day = 74.4watts per kg). The procedure was to follow the standard ASTM C 1293 test but with the addition of microwave energy to vacuum sealed samples.

4. RESULTS AND DISCUSSION

4.1. ASTM C 1260

The plots of the ASTM C 1260 expansion results for mortar made with WY aggregate and the modified ASTM C 1260 with concrete made from the WY aggregate are presented in Figure 3. The initial rate of expansion was greatly accelerated by the samples with holes and cut sides. The 21 day expansions of the samples with holes were about 65% higher than the solid samples and 33% higher than the cut samples. The 14 day expansion (0.21%) of the standard test for the WY aggregate was achieved in about 100 days. The samples with holes achieved approximately 1/3 the standard 14 day expansion in 21 days.

Figure 4 shows the expansions for the WY RCA concrete with two different millruns of the same cement with equivalent alkali contents of 1.15% (cement A) and 1.37% (cement B). The higher alkali did not have a significant affect on early expansions. The ultimate expansion should be the same for all cements because of the unlimited alkali in the solution surrounding the samples. Comparing the 28 day expansions of the RCA and the WY aggregate (Figure 3) shows the expansion of the RCA concrete to be about 89 % of the solid samples expansion. This is most likely due to less total reactive aggregate and the compounding effect of the old paste in the RCA. The cube samples and the larger samples with holes showed accelerated expansions compared to the solid sample. The fact that the prisms with holes expand at an increased rate suggests the mechanism of expansion is significantly controlled by diffusion processes. The prisms with holes have a greater surface area for diffusion to occur and also reduce the diffusion path lengths, thus accelerating the process.

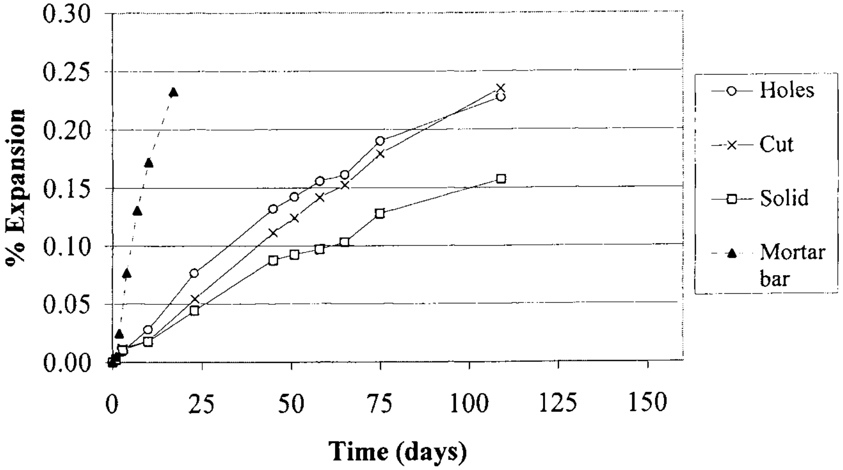

Figure 3. ASTM C 1260 expansions for mortar bars and concrete for WY aggregate.

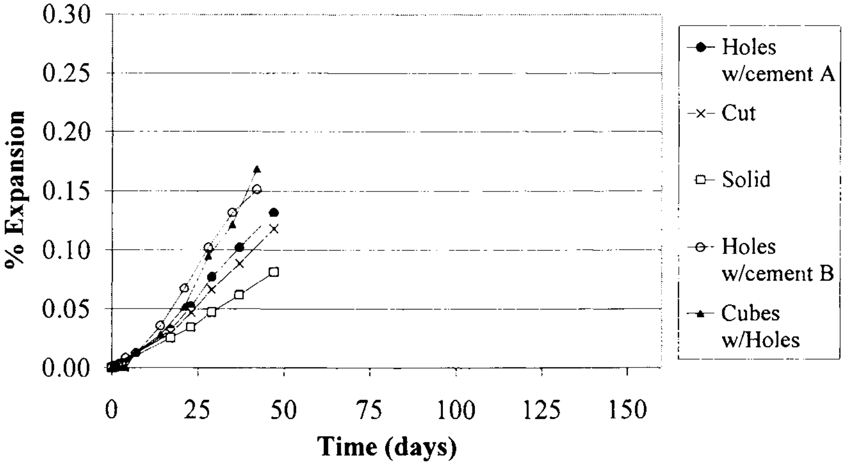

Figure 4. ASTM C 1260 expansions for WY RCA concrete.

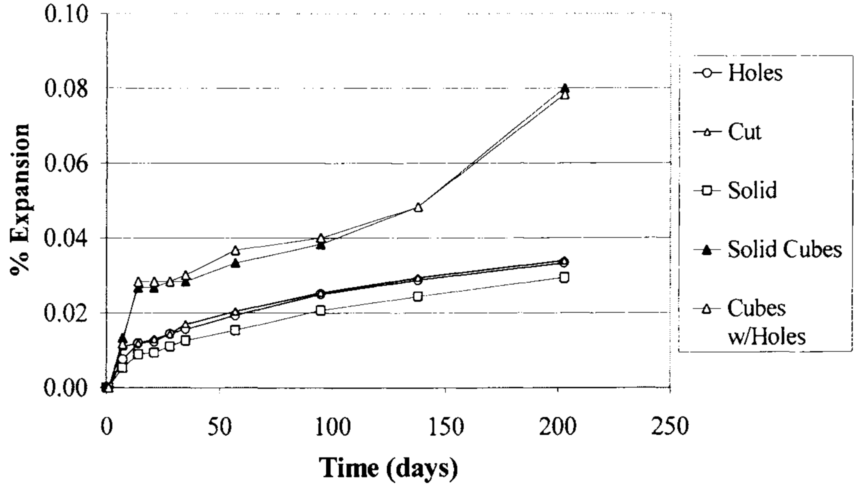

Figure 5. ASTM C 1293 expansions for WY RCA concrete.

4.2. ASTM C 1293 Test

The ASTM C 1293 data for the RCA concrete are shown on Figure 5. As with the ASTM C 1260 testing, the cut samples and samples with holes expanded at a higher rate than the solid samples. The cube samples expanded about 3 times more than the solid sample at early ages. Figures 6 and 7 show the relationship between expansion, mass increase and time. The cube samples expanded much more with less increase in mass than the larger samples.

Figure 8 presents the expansion data for a modified version of the ASTM C 1293 where the samples were sealed in an evacuated bag with 25 ml of water as previously described. The expansions, depending upon the shape, ranged from 21% to 63% higher than those of the standard test as shown on Figure 5. The variation caused by shape as well as the variation between samples was much less for the sealed samples. The cubes with holes showed greatly accelerated expansions of more than a factor of two at 21 days when compared to the larger prisms.

Figure 9 shows the relationship between expansion and mass increase. The solid sealed samples showed the least mass increase for a given expansion which was just opposite for the standard ASTM C 1293 test data where the cubes showed lower mass gain.

4.3. Microwave Energy

The effect of microwave energy is shown on Figure 10, and as with the other ASTM C 1293 tests, the small cubes show more expansion than the larger prisms. The expansions were in general slightly higher than the sealed ASTM C 1293 testing. Figure 11 shows the expansion as a function of mass increase. The samples with holes show higher mass increase than the solid samples. Comparing the microwave cubes with the sealed cubes in the 1293 suggests the effect of the microwave is not significant in increasing expansion. The microwave only appears to have an effect on increasing the expansion of the solid prisms. This could be due to the drying effect that the microwaves have on the smaller samples with holes. The overall effect is not significant in increasing expansion.

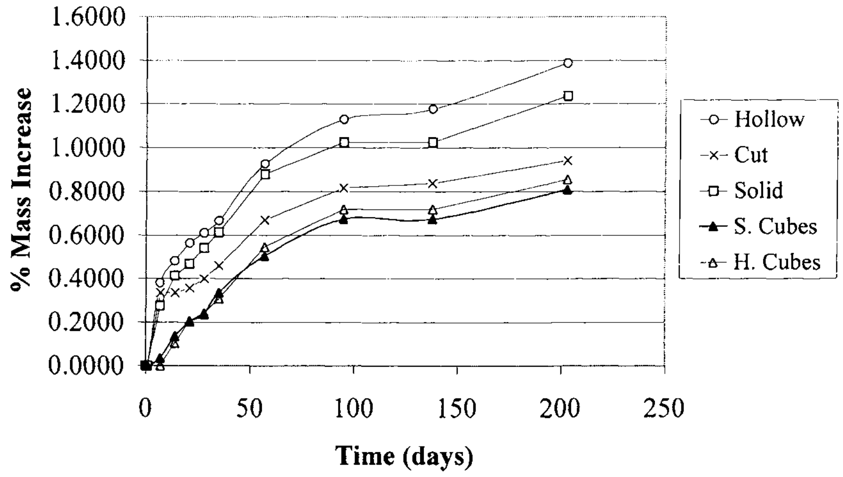

Figure 6. ASTM C 1293 mass increase for WY RCA concrete.

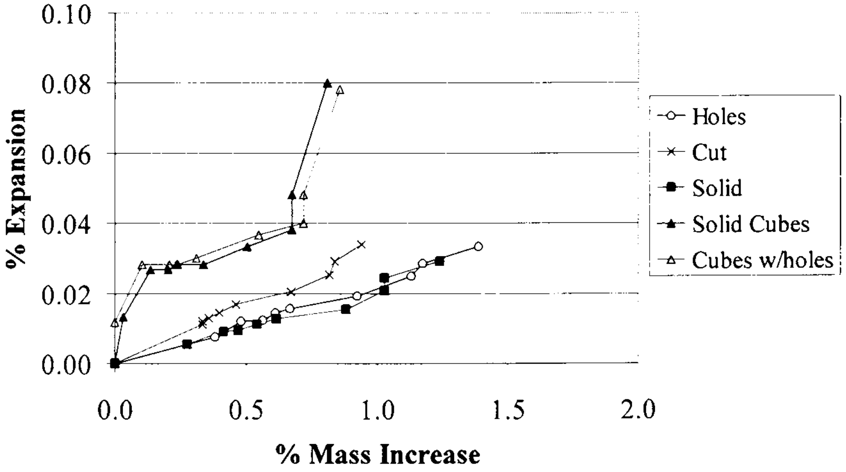

Figure 7. ASTM C 1293 sealed prism expansions for WY RCA concrete.

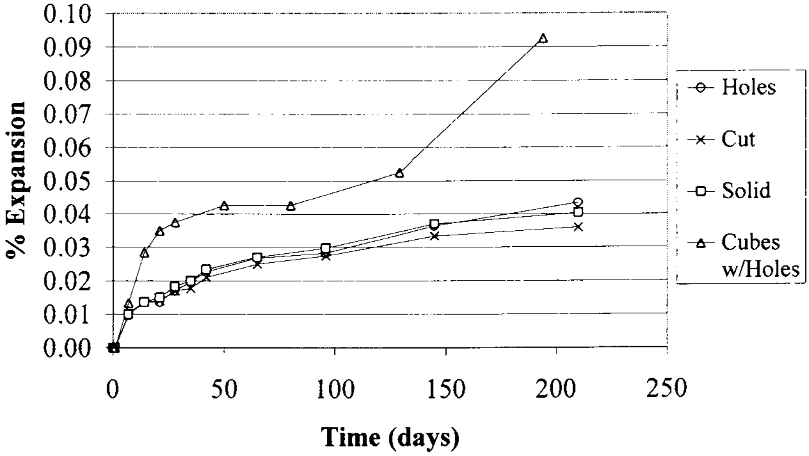

Figure 8. ASTM C 1293 sealed prism expansions for WY RCA concrete.

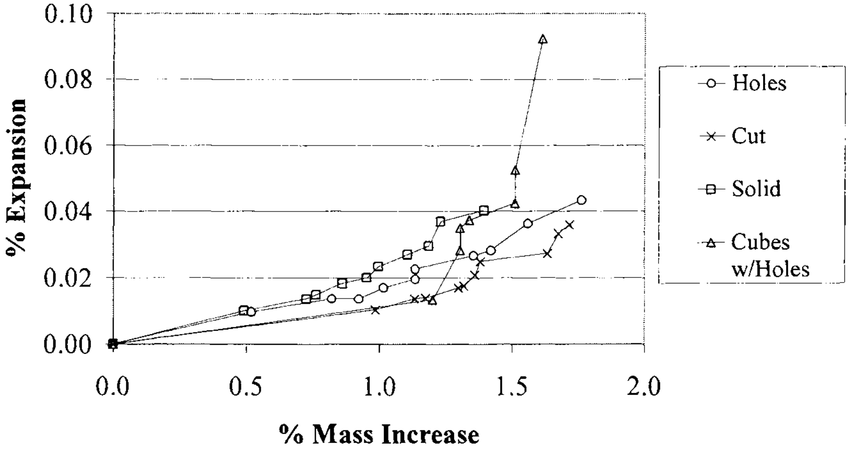

Figure 9. ASTM C 1293 sealed prism expansions versus mass increase for WY RCA concrete.

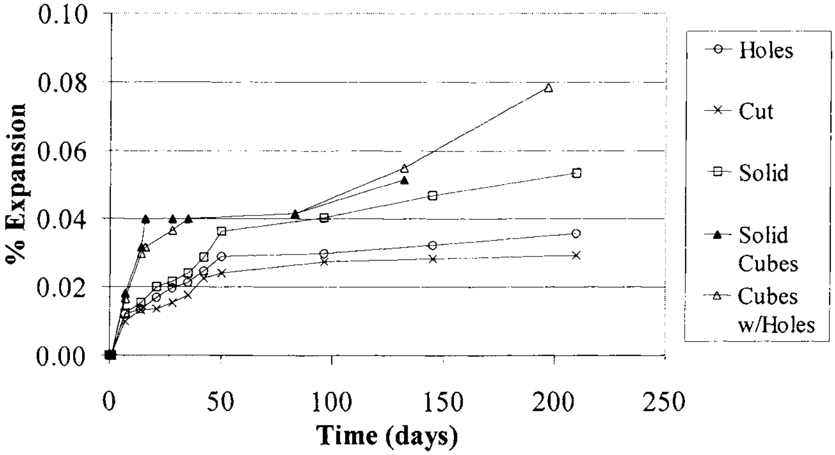

Figure 10. ASTM C 1293 sealed microwave prism expansions versus mass increase for WY RCA concrete.

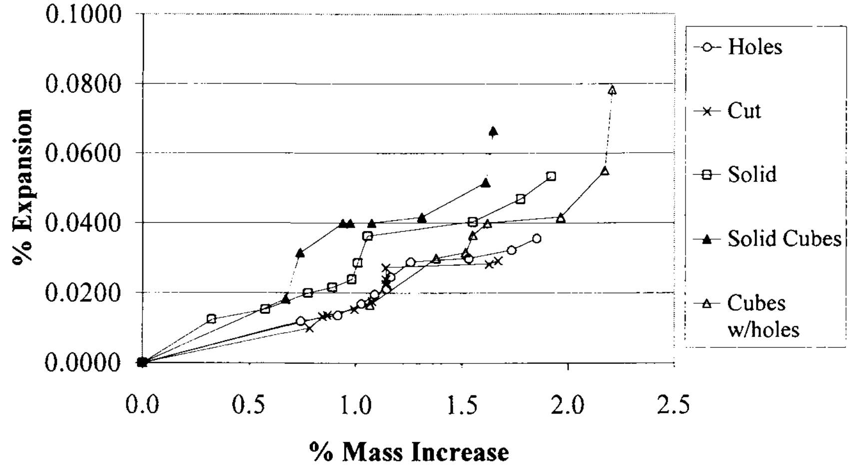

Figure 11. ASTM C 1293 sealed microwave prism expansions versus mass increase for WY RCA concrete.

5. CONCLUSIONS

Based on these data the following conclusions seem appropriate for the accelerated ASR testing of RCA concrete:

1. RCA samples show smaller expansions with modified ASTM C 1260 testing than the original aggregate does with the standard ASTM C 1260 testing.
2. Concrete cubes significantly accelerate expansions in the ASTM C 1260 and the ASTM C 1293 test compared to solid prisms.
3. Increase of mass during testing varies as a function of sample shape, moisture testing state, and type of testing.
4. Prisms sealed in evacuated plastic bags show increased expansions with less variation between samples than in the standard ASTM C 1293 test.
5. Low levels of microwave energy slightly increase expansion as compared to sealed ASTM C 1293 testing.
6. The combination of using RCA concrete cubes sealed in evacuated plastic bags is a viable means of effectively increasing the rate of expansion in the ASTM C 1293 test.

ACKNOWLEDGMENTS

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

The use of fly ash as a substitute of cement in microsurfacing

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The paper describes the results of the addition of fly ash, a well-known by-product of hydroelectric units, in microsurfacing as a substitute of cement. Microsurfacing is a high quality slurry seal and is extensively used, in some countries, for the provision and restoration of skid resistance of the road surface. Microsurfacing technology requires the addition of filler additive (most often cement) in order to control the breaking time of the emulsion.

This paper examines the breaking time of the emulsion, the cohesion and the abrasion resistance of microsurfacing material with fly ash in comparison to microsurfacing with cement.

The results have shown that the fly ash is more active than cement, which is an advantage, especially when microsurfacing is applied at low environmental temperatures. Additionally, due to the higher activity of the fly ash the required amount of additive is less than cement. This has a positive effect on the overall filler content in the case of high filler content in the original aggregate mixture. Therefore, the fly ash by-product, the disposal of which causes a great environmental problem, can be used as an alternative material to cement in microsurfacing. The use of fly ash in microsurfacing also reduces its overall cost.

1. INTRODUCTION

Microsurfacing [1], like its parent product slurry seal [2], is a mixture of dense graded aggregate, asphalt emulsion, water and mineral fillers. While conventional slurry seal is used around the world as an economical treatment for sealing and extending the service life of both urban and rural roads, microsurfacing has added capabilities, thanks to the use of high-quality, carefully monitored materials, including advanced polymers and other modern additives. So today, microsurfacing is defined as a polymer-modified, quick setting, cold-slurry paving system. Microsurfacing does not require extensive drying prior to opening to traffic and it can be placed during a wide range of climatic conditions.

The components are proportioned and blended at the rear end of a microsurfacing paver and distributed on the paver with a heavy duty ''spreader box'' equipped with augers and adjustable strike-off. The use of microsurfacing is rapidly growing for maintenance of highways, high traffic streets and airports.

Microsurfacing has become one of the most cost-effective and comprehensive pavement maintenance practices, available with plenty of benefits like:

- complete pavement restoration to a newly paved uniform black color appearance.
- quick set-up for application on high volume, high speed pavements
- minimal disruption to travelling public and local residents
- it provides a durable, highly skid resistant surface
- the system is considered as environmental-friendly since there is a significant conservation of resources (asphalt, aggregates) and it is applied in ambient temperatures with only evaporation of water.

Microsurfacing is normally specified and designed according to ISSA recommendations [3].

The mineral filler, which is added in the mixer by a discrete delivery bin, could be either limestone filler or most often cement. It has a double role to play in the mixture: to bring the percentage of filler to the required amount and to accelerate the breaking time of the modified asphalt emulsion (the alkaline-based filler reacts with the acid-based emulsion).

The results from the replacement of cement, as filler additive, by fly ash, which is a by-product from coal-fired electric power generation, are presented in this paper. This replacement can result in significant technical and economical benefits.

2. EXPERIMENTAL STUDY

2.1 Materials

a) Aggregate

The aggregate used, coarse and fine, was produced from crushing a diabase rock. The characteristic properties of the aggregate were as follows:

PSV: 56, AAV: 5, Los Angeles: 22%, ACV: 15%, Water absorption: 0.5%, Specific gravity: 2.82 gr/cm^3 and Bitumen coating > 95%.

The gradation of the aggregate mixture was within the specified limits as determined by ASTM [2] or ISSA [3] for Type 3 mixture. The actual gradation of the aggregate mixture is as shown in Table 1.

b) Bitumen emulsion

The bitumen emulsion used was a cationic bitumen emulsion modified with latex. Its characteristics, which meet the requirements of AASHTO M 316-96 [4] specification, are shown in Table 2.

c) Mineral fillers

The mineral fillers used were ordinary Portland cement (OPC) and pulverized fuel ash (PFA). The ordinary Portland cement was type I 45, according to Greek specification and its composition is as shown in Table 3.

Table 1
Aggregate mix gradation

Sieve size (mm)	Percentage passing (%)
12.5mm	100
5.0mm	82
2.36mm	52
1.18mm	36
0.600mm	26
0.300mm	18
0.150mm	12
0.075mm	9

Table 2
Characteristic properties of latex modified bitumen emulsion

Tests	Limits	Results
a. Tests on emulsion		
Viscosity, Saybolt Furol at 50° C, s	100 – 400	125
Particle charge	Positive	PH≈2.5
Sieve test, %	< 0.1	0
Residue, by evaporation, %	> 65	66
b. Tests on residue from evaporation test		
Penetration, 25° C, 100gr, 5 sec	> 30	55
Elastic recovery, %	> 50	58
Polymer content, %	> 2.5	3
Solubility in trichloroethylene, %	> 97.5	> 97.5

The PFA was from a coal-fired electric power generation plant situated in Ptolemaida, Northern Greece and its characteristics and composition are shown in Table 3.

Table 3
Composition of mineral fillers

Characteristics/composition	OPC	PFA
SiO_2	21.9	41.4
Al_2O_3	6.7	10.1
Fe_2O_3	2.4	3.4
CaO	61.7	37.8
MgO	2.0	3.5
K_2O	1.1	6.5
Na_2O	0.3	1.4
SO_3	3.0	
LOI	1.52	2.75
CaO (free)	1.32	11.4
Fineness (cm^2/gr)	3.300	4.740

2.2 Mix Design

The mix design was performed according to ASTM [2] and ISSA [3] specifications. The laboratory design concerned six representative mixes with OPC as added filler and six mixes with PFA as an alternative added filler. The percentage of either OPC or PFA in the microsurfacing mixtures was 0%, 0.5%, 1.0%, 1.5%, 2.0%, 2.5% by weight of aggregate mixture.

The constituents of the mixture per 100gr of aggregate, after performing the constituent test, were as follows:

Aggregate : 100 gr
Modified asphalt emulsion : 12 gr
Water : 12 gr
Mineral additive : 0 – 2.5 gr

2.3 Testing

The twelve different mixtures were tested for the determination of set time and the weight loss by wet track abrasion test, according to ASTM [2] and ISSA [3] specifications. The mixing temperature which affects the set time, for all mixtures produced, varied and it was 15°C, 25°C and 35°C. The humidity during mixing was kept constant, in all cases, and equal to 50%.

3. RESULTS AND DISCUSSION

3.1. Set time

The results obtained for the set time are as shown in Figure 1. As it can be seen, for both types of added filler the set time reduces as the mixing temperature and/or the amount of filler increases. Furthermore, when PFA is used the set time is less than that when OPC is used. The lower set time obtained when PFA is used is attributed to the higher percentage of free CaO present in the PFA (11.4%) in comparison to the percentage of free CaO in the OPC (1.32%).

The lower set time (initial breaking of the mixture) when PFA is used, which effectively reduces the cure time (final breaking of the mixture) of the mixture, is in advantage since the microsurfacing ultra thin layer can open to traffic quicker. This is more important when the works are carried out at low air temperatures, for example during winter months or in countries with generally low air temperatures.

Furthermore, since added filler is always needed to control the breaking time of the emulsion, lower amount of PFA filler is required to be added in order to shorten the set time. This is due to its higher activity compared to OPC. Additionally, the addition of lower amount of filler does not result in a total filler content outside the specified limits. Being outside the recommended limits for total filler content is possible when the fine aggregates contain high amount of filler.

3.2 Wet track abrasion test

Wet track abrasion test, after one hour soaking, was carried out on all microsurfacing mixtures prepared and the results are as shown in Figure 2.

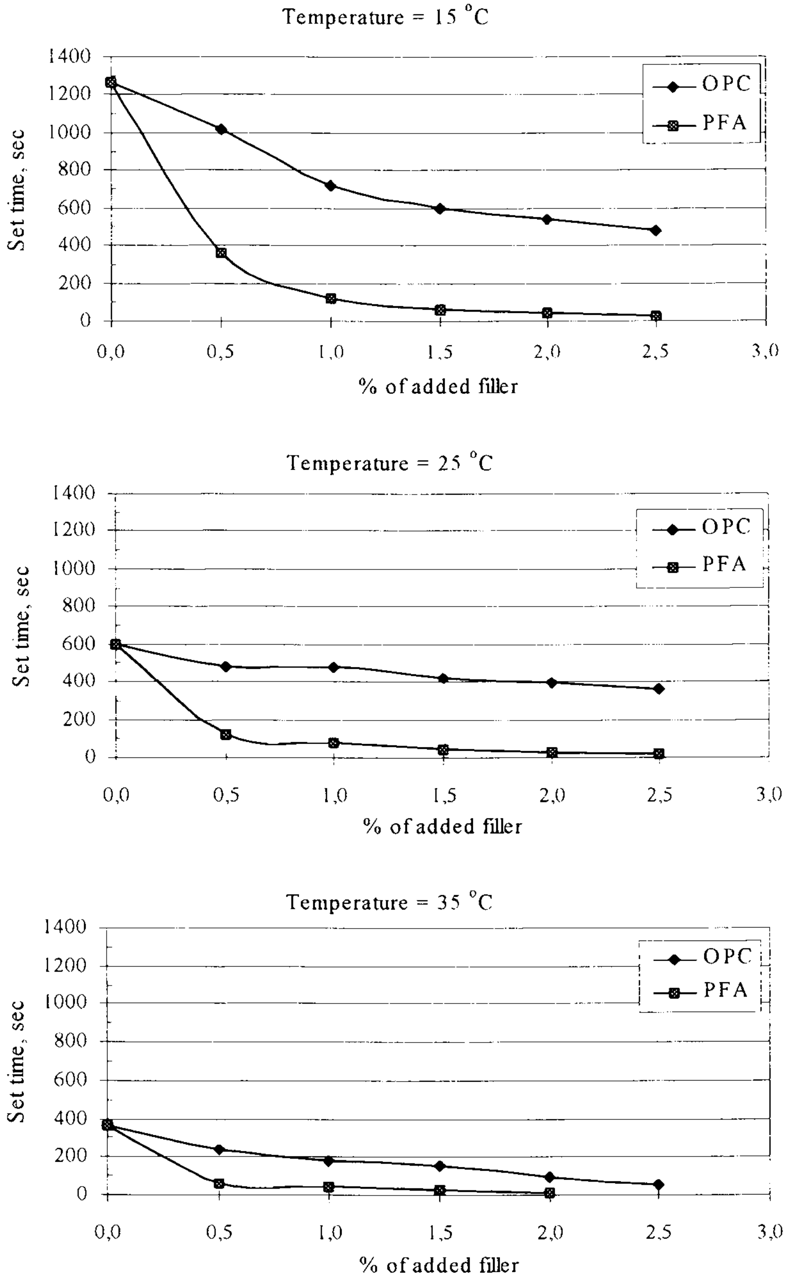
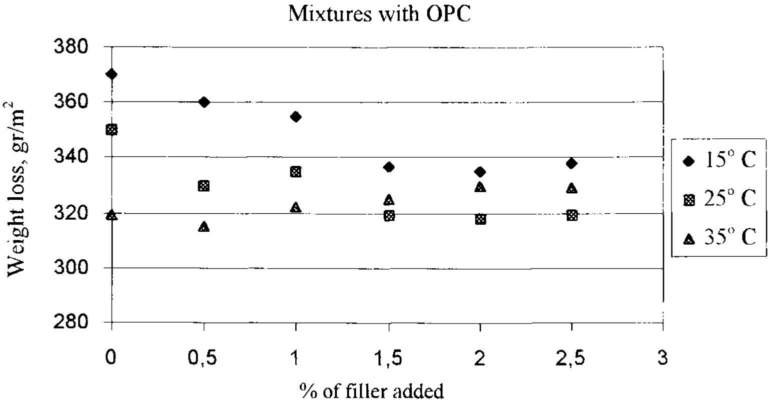


Figure 1. Set time Vs % of added filler (Mixing temperature = 15° C, 25° C and 35° C)



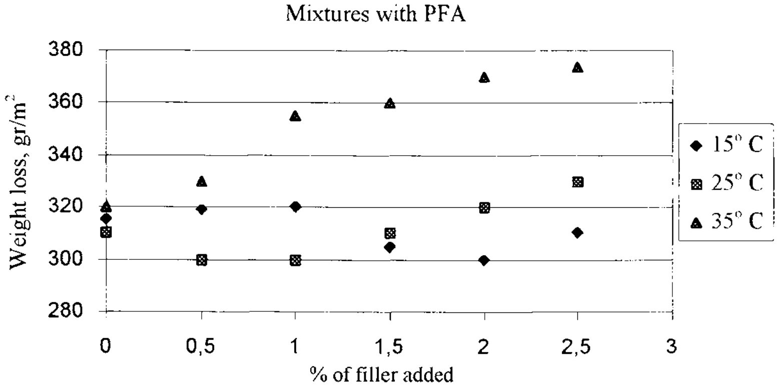


Figure 2. Weight loss after wet track abrasion test

All mixtures, irrespective of set time, gave results that were well below the maximum permissible weight loss, which is 538 gr/m2. Generally, all mixtures with OPC or PFA added filler mixed at 15°C and 25°C showed almost the same weight loss after wet track abrasion. However, for the mixtures with PFA mixed at 35°C, the weight loss increased slightly as the percentage of added filler increased. This, in conjunction with results obtained with the mixtures with low percentage of OPC mixed at 15°C, suggests that the set time been either very short or too long, respectively, affects the cohesion of the mixture and hence its performance in wet track abrasion test. For the latter to be justified properly, further investigation is required.

4. CONCLUSIONS

The outcome of this investigation shows that the replacement of OPC, normally added in microsurfacing mixtures mainly for controlling the breaking time of the bitumen emulsion, has some advantages. Since PFA is more active than OPC, the breaking time can be shortened with a lower amount of filler added. This allows microsurfacing to be opened to the traffic sooner or be laid at lower environmental temperatures, hence extending the construction seasonal period. Additionally, the use of PFA instead of OPC is more cost effective when one considers the lower initial cost and the environmental intrusion caused by the production of both materials and the disposal of PFA byproduct.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Composition of Organic Matter in Bottom Ash from MSWI

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A rough estimate of the bulk organic matter composition in bottom ash was made in this study. This estimate is based on the earlier results of characterisation of aqueous and non-aqueous bottom ash leachates by different analytical techniques, such as TOC measurements, gas chromatography-mass spectrometry, size exclusion chromatography, UV-VIS spectrophotometry, fractionation on XAD resins, and also on other data presented in the literature. These results suggest that cellulose and lignin are the major organic constituents of the bottom ash. Also fractions of water-soluble high- and low-molecular-weight substances as well as a fraction of organics, extractable with non-polar organic solvents were defined. In these extractable aqueous and non-aqueous fractions a number of individual organic substances have been identified.

1. INTRODUCTION

It is now increasingly been recognised that organic substances play an important role in the chemical behaviour of bottom ash. Despite this, very little is known about the bulk chemical composition of the organic matter present in bottom ash. That is because characterisation of organic substances in municipal solid waste incineration (MSWI) residues has so far been focused mainly on some highly toxic compounds, such as dioxins, which are present only in trace amounts and the total bulk composition of organic carbon in the bottom ash is still largely unknown.

The aim of this paper was to summarise the results of studies of the organic matter in bottom ash and give an overall estimate of the composition of bulk organic matter.

2. ROLE OF ORGANIC SUBSTANCES IN BOTTOM ASH

Municipal solid waste (MSW) itself is very rich in organic matter with the main constituents being paper, food waste, plastics, textiles, and wood. According to Chandler et al. [1] the total content of organic matter in MSW varies between 60 to 90%. Therefore MSW incineration has been found to be a very efficient waste handling method, which is done mainly for the reasons of volume reduction and energy recovery.

Incineration is usually performed at about 1000°C. Despite this temperature there is a fraction of un-combusted organic matter still present in the incineration residues (mainly in bottom ash) and the amount of residual organics largely depends on the incinerator operation conditions and on the original composition of the waste. When the bottom ash is deposited of or used as a secondary raw material, mainly in construction applications, these organics can have several effects on the behaviour of the bottom ash. Organic substances can:

i) lead to toxicity and even mutagenicity in some cases [2, 3]. As already mentioned in the introduction, attention so far has been mainly focused on a few classes of highly toxic compounds that are only present in trace amounts in the incineration residues. These classes include polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenols (PCBs), and polyaromatic hydrocarbons (PAHs);

ii) induce complexation of dissolved organic carbon (DOC) with metals [4, 5] or other toxic organic compounds, such as PAHs [6], thereby enhancing the mobility of these species and a possible release to the environment. The complexation of metals has been particularly noted in case of Cu since it is comparatively easy to measure this metal in solutions and it has large affinity to formation of coordination compounds;

iii) cause the release of CO_2 during microbial degradation, thus decreasing the pH, which will in turn reduce the buffer capacity of the bulk waste material [7, 8];

iv) impose reducing conditions that lower metal leachibility due to the formation of insoluble phases, such as metal sulphides [9].

There might also be other, yet unidentified effects of organic substances on the behaviour of bottom ash. For example, there are no reported studies on the long-term transformations and fate of organics in the bottom ash and what might be the consequences of these transformations. One of such possible transformations could be degradation/alkaline hydrolysis of phthalates to monoesters and phthalic acid with analogy of similar processes noted in the landfilled MSW [10]. Phthalic acid monoesters have been accused for the disturbing effects in hormones [11, 12].

In the light of the above-described important role of residual organics present in the bottom ash, comparatively little is known about the bulk composition of this fraction. Results from published studies on this subject will be summarised below.

3. CHARACTERISATION OF ORGANIC MATTER

Loss-on-ignition (LOI) is often being used as an indicator of the content of organic matter in bottom ash. In a study performed on 26 fresh and stored bottom ash samples from four Swedish incinerators sampled on four occasions at 3-month intervals the LOI was in the range of 26-117 g/kg [13]. Somewhat surprisingly there was found no correlation of the LOI with the amounts of leached organic carbon from the same samples. Meima and Comans [14] observed that dissolved organic carbon (DOC) concentrations in bottom ash extracts increased strongly with decreasing liquid-to-solid phase ratios, indicating that DOC leaching is controlled by the amount of soluble organic material present. This suggests that the LOI was not representative of the organic matter content in the previously mentioned study.

The method of LOI has been adopted from its usage on other types of samples, such as sewage sludge and sediments. However, the matrix of bottom ash is considerably different from these materials and there are several other factors, which might contribute to the LOI in

Table 1
Total organic carbon content in bottom ash

Organic carbon content (g/kg)	Source
10-20	[7]
4.8-13	[17]
10-14	[18]

bottom ash: there can be present elemental carbon in the ash, which will start to oxidise at 400°C [15, 16]; entrapped water and tightly bound water of hydration will not be released at drying temperatures but will escape at 550°C; the measurements will be influenced by the inherent inhomogeneity and the highly hygroscopic character of the ash [1]. In fact, it has been suggested that only up to 60% of the LOI is organic matter (personal communication quoted in [1]).

In Table 1 there are shown results of the total organic carbon (TOC) content in bottom ash. It can be observed that these values are generally lower than the values of the LOI in the above-mentioned study.

The fraction, which has the most practical importance in characterisation of bottom ash performance, is the organic carbon fraction soluble in water, since bottom ash is expected to be constantly exposed to the atmospheric deposition and percolating water. The results of water-leachable DOC content in bottom ash are summarised in Table 2.

The organic carbon seems to be rapidly released to the aqueous phase; approximately 90% of the maximum amount of DOC was released during the first 24 hours and about 60% within the first 10 minutes [19].

What are then the individual substances comprising the DOC? A study of fractionation of aqueous bottom ash extracts on XAD-4 and XAD-8 resins indicated that approximately half of this carbon is composed of, most probably, low-molecular weight (LMW) hydrophilic organic acids, one third represents somewhat more hydrophobic acids, and there is present also a fraction of few percent of non-acidic hydrophobic compounds. Gas chromatography-mass spectrometry (GC-MS) analysis of these fractions has revealed several individual compounds representing fatty acids, dicarboxylic and aromatic acids, hydroxyacids, monosaccharides, phthalates, and several other hydroxy compounds, mainly glycerol [21, 20].

Table 2
Dissolved organic carbon (DOC) leachable to the aqueous phase from bottom ash.

pH	DOC (mg/kg)	Source
10.7-10.9	650	[6]
11.5-11.7	103	Stämpfi et al., 1990 quoted in [7]
11.4-11.7	44	Ibid
-	91.8	[3]
10.32	460	[14]
8.82	205	Ibid
9.3-8.8	170	[19]
~13 (0.1 M NaOH)	375	[20]
~13 (0.1 M NaOH)	210-1870	[13] fresh bottom ash
~13 (0.1 M NaOH)	160-570	[13] bottom ash stored in open

In [21] it was shown that there is an evidence suggesting the presence of humus-like, high-molecular-weight (HMW) organic substances in aqueous (alkaline) bottom ash extracts, mostly contained in the XAD-8 fraction. This was done by spectrophotometric (UV-VIS) and molecular size (size exclusion chromatography) studies. Belevi et al. [8] reported a similar molecular size distribution pattern with large fraction at around several hundred daltons and a smaller, more diffuse fraction at several thousand daltons. Knowing the metal complexin capacity of humic substances, it can be hypothesized that it is the HMW, humic-like fraction of the soluble organic matter that is responsible for the complexation of metals.

In order to investigate the non-polar organic substances the extraction can be performed using non-polar organic solvents (such as dichloromethane, toluene and others). Approximately 100 compounds have been detected in such extracts and most of them identified [21, 20]. The predominant compound groups were n-alkanes, saturated fatty acids, polyaromatic and aromatic compounds, and phenolic compounds. Detected compounds included also several PAHs and phthalates, which are listed as priority pollutants. Similar compounds as in these two studies have been also found by Priester et al. [16]. It is interesting to note that the amounts of organic carbon extracted by non-polar organic solvents (approx. 20 mg/kg) are only a small fraction of the total content of organic carbon in the bottom ash (see Table 1). The dioxins and PCBs also belong largely to this fraction.

A noteworthy observation has been made by Pavasars et al. [21] where isosaccharinic acid (ISA), a product of alkaline degradation of cellulose [22] and several oxidation products of lignin were detected. These results suggest that there are un-combusted residues of cellulose and lignin present in the MSWI residues. According to Chandler et al. [1] about 40% of MSW is composed of paper and 30% of woody or plant material, most likely as food waste. It is possible therefore that cellulose and lignin comprise the major part of organic matter in bottom ash, since these materials are present in large amounts in the original MSW. Furthermore, lignin and cellulose are not soluble in water or non-polar organic solvents that would explain why only a small amount of organic carbon can usually be leached with aqueous or non-polar organic solvents.

4. COMPOSITION OF THE BULK ORGANIC MATTER

Based on the results described above it was attempted to make a very rough estimate of the total composition of organic matter in bottom ash. Naturally, the composition of bottom ash is widely varying and this estimate may only give the main principles of the organic matter composition. For this purpose it was assumed that the organic carbon content in bottom ash is 10 g/kg (see discussion above and the results in Table 1). Further, it was assumed that there is a water-soluble organic matter of 0.5 g/kg (see Table 2) and 30% of this fraction represent HMW, possibly humic-like substances. Approximately 20 mg/kg of organic carbon are extractable with non-polar organic solvents and the rest of organic matter is composed of cellulose and lignin. Assuming the same proportions of woody plant material (food waste) to paper in bottom ash as in the original MSW (30% to 40%, see above) and the cellulose-to-lignin ratio in woody plant material 1:1, the total organic matter composition appears as shown in the Figure 1.

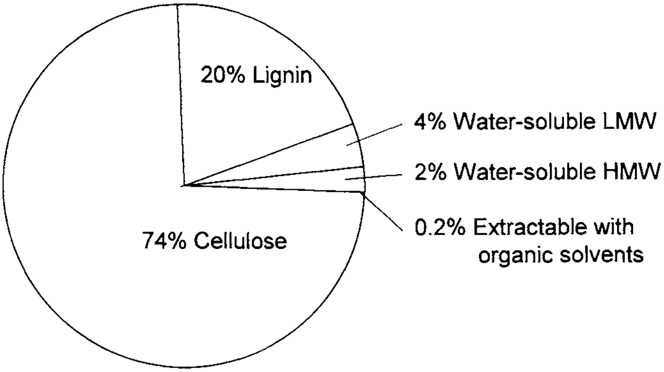

Figure 1. An example of the total bulk composition of organic matter present in bottom ash.

It must be stressed again that Figure 1 represents only the general principle and the organic matter composition in bottom ash will largely differ from sample to sample. Nevertheless, this might serve as a point of departure in further investigations of organic matter in bottom ash.

5. CONCLUSIONS

Organic matter in bottom ash is mainly composed of un-combusted cellulose and lignin, which are contained in large amounts in the original MSW as paper and woody or plant material. A few percent of the total bulk organic matter are extractable with water of which about one third represent HMW, possibly humic-like substances. There is also present a small organic matter fraction, which is extractable with non-polar organic solvents. Several individual organic substances have been identified in the extractable fractions. The aqueous phase contains compounds representing fatty acids, dicarboxylic and aromatic acids, hydroxyacids, monosaccharides, phthalates, and several other hydroxy compounds, mainly glycerol. The predominant compound groups in non-polar organic extracts were n-alkanes, saturated fatty acids, polyaromatic and aromatic compounds, and phenolic compounds. Detected compounds included also several PAHs and phthalates.

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Waste Materials in Construction
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Environmental impact of ferrochrome slag in road construction

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ABSTRACT

Vargön Alloys in Western Sweden is one of the largest producers of ferrochrome slag in Europe. Ferrochrome slag is a by-product from the production of ferrochrome, an essential component in stainless steel. Extensive tests have been carried out on the physical properties of the ferrochrome slag from Vargön Alloys e.g. brittleness, flakiness, mass wasting, Los Angeles value and capillary properties, and it was found to be highly suitable as road construction material. The current level of production of ferrochrome slag is about 150,000 tonnes per year. In untreated conditions the bulk density of the slag is around 1.5 t/m^3 and the volume generated can be up to 100,000 cubic metre per year. The slag is crushed and sold in different fractions between 0-100 mm.

The composition and leaching tests of the ferrochrome slag show that the chromium content is high, 1-3%, although leaching under normal conditions is very low. With the exception of potassium (K), which had a potential leaching capacity (availability test) of around 16 %, the leaching of chromium, nickel, zinc and other elements was just a few per cent. However, all these tests were conducted in the laboratory. What happens out in the field, under the influence of acid rain and biological activity, and how does this compare with the laboratory results?

To answer this question an investigation was carried out to study the environmental impact of ferrochrome slag in roads that were built in 1994. The investigation includes soil sampling (total content) and groundwater analysis (filtered and non-filtered samples). In addition, a new method involving the bio-uptake of chromium and other metals by the roots of the dandelion (*Taraxacum officinale)* was tested. The results show that there was a low migration of particles from the slag to the underlying soil and that the leaching into the groundwater was also low for all the elements analysed. However, there seemed to be a significant uptake of Cr by plants growing with their roots in the slag. An investigation of plant uptake was an important complement to laboratory leaching tests on alternative materials.

1. INTRODUCTION

Vargön Alloys in Western Sweden is one of the largest producers of ferrochrome slag in Europe. Ferrochrome slag is a by-product from the production of ferrochrome, an essential component in stainless steel. The physical properties of ferrochrome slag from Vargön Alloys have been extensively tested e.g. brittleness, flakiness, mass wasting, Los Angeles value and capillary properties, and it was found to be very suitable as road construction material. The current level of production of ferrochrome slag is about 150,000 tonnes per year. In untreated conditions the bulk density of the slag is around 1.5 t/m^3 and the volume generated is about 100,000 cubic metre per year. The slag is crushed and sold in fractions from 0 to 100 mm.

The slag is attractive as construction material due to its excellent technical material properties. However, environmental concerns has been raised about the content and leachability of heavy metals, especially chromium (Larsson 1995; Fällman & Hartlén 1997).

The chemical composition of the ferrochrome slag includes three major elements; silicon (Si), manganese (Mg) and aluminium (Al). Together with their oxides these components make up 83 % of the slag (Larsson 1995). Among the heavy metals, the chromium content (Cr) is particularly high at about 3 %, which is about 1,000 times the concentration in the natural soils of the region (Melkerud et al. 1992). The concentrations of Co, Ni, Sn and W are about 100 times higher than in the natural soils.

Leaching tests with salt seawater and pH-adjusted water reveal low leachability from the slag for most elements. Concentrations in the leachate from the slag are often in the same order as leaching from natural till sediments (Larsson 1995; SGI Internal database). In salt water only Mn showed any significant leaching from fresh surfaces (Cnubben et al. 1998). A potential leachability test (availability test) shows low leaching of all elements, except for potassium (K) which has a potential leaching capacity (availability test) of 16 %, (Larsson 1995). The leachability of Cr was 0.03-1.7 % of the total content; Ni 4.6-6.4 % and Zn 3.3-5.9 %. However, all these tests were performed in the laboratory. The question is what happens out in the field, under the influence of acid rain and biological activity, and how does this compare with the laboratory results?

The aim of this project was to study under full-scale field conditions the environmental impact of the ferrochrome slag on plant uptake, groundwater and soil composition and to compare the results from the field sites with the laboratory investigations.

2. MATERIAL AND METHODS

2.1. Field sites

Two roads with ferrochrome slag in the construction, with and without an asphalt covering, were used as field sites in this study. The covered site was a 6 km long open road, which was reconstructed in 1994. Half the distance was reconstructed with approximately 20,000 tonnes of ferrochrome slag on top of the old road separated by a geotextile (see Figure 1). The other half of the road was reconstructed with conventional macadam material (reference site). The top was covered with an asphalt layer, although the sides of the road were left uncovered and exposed to stormwater runoff and infiltration. The soil cover at the test site was about 3.5 m deep and of a sandy texture. Two polyethylene, high-density (PEHD) groundwater pipes were installed, at 1 m (3.45 m depth) and 4 m (3.04 m depth) from the asphalt edge (see Figure 1). The pipes were installed in direct contact with the ground material, without any sand filter.

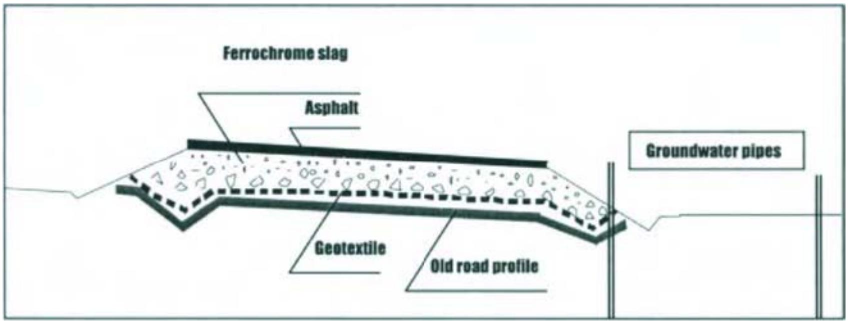

Figure 1. Investigation site with asphalt cover. Road 1018, section 4/600. The road is 6 m wide and built up of coarse slag (5-20 cm) of varying thickness on top of a polypropylene and polyester geotextile (Viacon SG 40/40) and covered with a 70-80 cm layer of finer slag (8-16 mm). The geotextile is highly permeable and does not obstruct infiltration.

The uncovered, open, site was a small 300 m long road and a parking area, built on natural forest ground in the winter of 1996. The road was constructed in two layers, with a total of 5,000 tonnes of ferrochrome slag. A layer of 0.2 m coarse slag was covered by a 0.25-0.3 m layer of crushed slag (0-8 mm). The road is situated in broken terrain, with a high proportion of bare or almost bare bedrock, and with a soil cover of till and gravel. Groundwater pipes (PEHD) were installed in the parking area at a depth of 1.63 m and 4 m from the road, in sandy till sediments at a depth of 1.75 m. The total composition of the ferrochrome slag was assumed to be the same as in the 1995 tests, see Table 1.

2.1. Soil sampling and analysis

An analysis was made of the total composition of soil samples collected from two profiles just outside the asphalt edge at the covered site. Samples were taken from two levels in the natural ground material below the slag; 0-5 cm below the ground surface (corresponding to the A_0 horizon) and 10-15 cm below the surface (the A_{1-2} horizon). Samples were pulverised in an agate mill, digested in a multi-acid digestion (HF, HNO_3, $HCLO_4$ and HCl) and analysed by Inductively Coupled Plasma Emission Spectrometry (ICP AES), (ICP80, XRAL Laboratories, Canada).

2.2. Sampling and analysis of plants

The bio-uptake of chromium and other metals by plants was analysed in the roots of the dandelion (*Taraxacum officinale*). The dandelion was chosen because it is common and because it has one deep root that covers a large part of the soil profile and it is easy to wash it free of soil particles. Plants growing in the slag were sampled along the roads at both the covered and uncovered sites. Plants growing in the macadam on the reference road at the

Table 1.
Total composition of Vargön Alloys ferrochrome slag as an average of two measurements *(Larsson, 1995)*.

Element	Unit		Element	Unit	
Fe	%	2.87	Cr	ppm	27,100
Ca	%	2.46	Cu	ppm	18.2
Si	%	13.6	Hg	ppm	<1.83
Mg	%	17.85	La	ppm	<12.2
Mn	%	0.1336	Mo	ppm	<6.09
Al	%	13.0	Nb	ppm	<12.2
P	%	0.0177	Ni	ppm	542
Ti	%	0.196	Pb	ppm	<8.42
K	%	0.185	Sc	ppm	17
Na	%	0.289	Sn	ppm	62.6
S	%	0.461	Sr	ppm	88.5
			V	ppm	49.1
As	ppm	<1.83	W	ppm	620
Ba	ppm	189	Y	ppm	9.73
Be	ppm	1.61	Yb	ppm	1.37
Cd	ppm	<2.28	Zn	ppm	132
Co	ppm	49.1	Zr	ppm	43.3

covered site were also sampled. At each sampling location a reference sample was collected 3 m from the slag - still affected by the traffic but not directly by the road material. Each sample was made up of ten plants with equally long leaves and roots approximately 20 cm long. A total of 120 plants were collected.

The samples were carefully washed with clean drinking water and dried in paper bags at room temperature for two months. The dry roots were pulverised by hands, wearing rubber gloves that were changed for each new sample. Test portions of 2.0 g pulverised sample were digested in 20 ml HNO_3 acid (10 ml conc. HNO_3 plus 10 ml 7M HNO_3) and heated to 100 °C for 40 minutes. After sedimentation for 5 h and decanting and dilution with deionised water, the composition was analysed by ICP-MS. The sample preparation and analysis were carried out by Swedish Geological Survey. The results were evaluated by an analysis of variance (ANOVA).

2.3. Groundwater sampling and analysis

Groundwater samples were taken three times at each location during the summer of 1999 - June 18, July 14 and August 12. At every occasion the groundwater pipes were emptied ones before sampling. The temperature, pH and redox potential were measured directly. Part of each sample was filtered directly (0.45 μm cellulose acetate filter). Unfiltered and filtered sub-samples were acidified to a pH of below 2 by the addition of approximately 0.5 ml concentrated HNO_3 to a 100 ml sample. Filtered and non-filtered groundwater samples were analysed for metals by ICP-MS (method MS200, XRAL Laboratories).

3. RESULTS

3.1. Soil contamination

An evaluation was made of selected elements (Cr, Co, Ni, Sn and W) that occur in the slag at elevated concentrations (about 100 times or higher) compared with the natural soils in the region. The total contents of the samples taken from under the slag at the covered site are presented in Table 2. The content in these samples of Sn and W were below the detection limit of 10 mg/kg. A comparison with the geochemical atlas of Swedish forest soils (Melkerud et al. 1992) shows that none of the elements studied revealed a positive deviation. The chromium content is in the range of medium to low for the region, whereas all other elements had low concentrations.

Table 2.
Content of selected elements (mg/kg) in soil samples from under the slag from two profiles at the covered site road. The detection limit was 1 mg/kg for Cr, Co and Ni.

Sample	Depth (m)	Cr	Co	Ni
Profile 1	0-0.05	40	1	9
Profile 1	0.10-0.15	38	3	8
Profile 2	0-0.05	32	<1	6
Profile 2	0.10-0.15	43	3	8

3.2. Plant uptake

The content of certain inorganic elements was analysed in the dandelion roots and the results are presented in Table 3, expressed as mg/kg dry substance. There was no significantly higher uptake of most elements ($p<0.05$) in roots growing in the macadam immediately beside the road compared with roots 3 m from the road at the reference part of the covered test site, except for Pb, which did show a non-significant tendency towards a higher uptake close to the road. It was concluded that samples close to the road were comparable with reference samples taken 3 m from the road without introducing too much uncertainty.

There was a relatively clear difference between the metal uptake for roots in the slag compared with the 3 m reference samples. Most obvious were the raised Cr-values, see Fig. 2. The average Cr-content in roots from the slag was at the covered site eight times higher than in the reference samples and at the open site 46 times higher than in the reference samples. However, the uptake of metals in the roots in the slag varied greatly and no statistically significant differences between slag samples and references could be found. One of the samples from the open site, for example, had comparatively very high concentrations of all the elements analysed except for Cd and Zn. Additional samples would be needed to determine the level of uptake of chromium from the slag. Molybdenum was taken up in the roots to a greater extent from slag than from macadam ($p<0.01$), and at the uncovered site molybdenum was taken up to a greater extent than at the covered site ($p<0.1$).

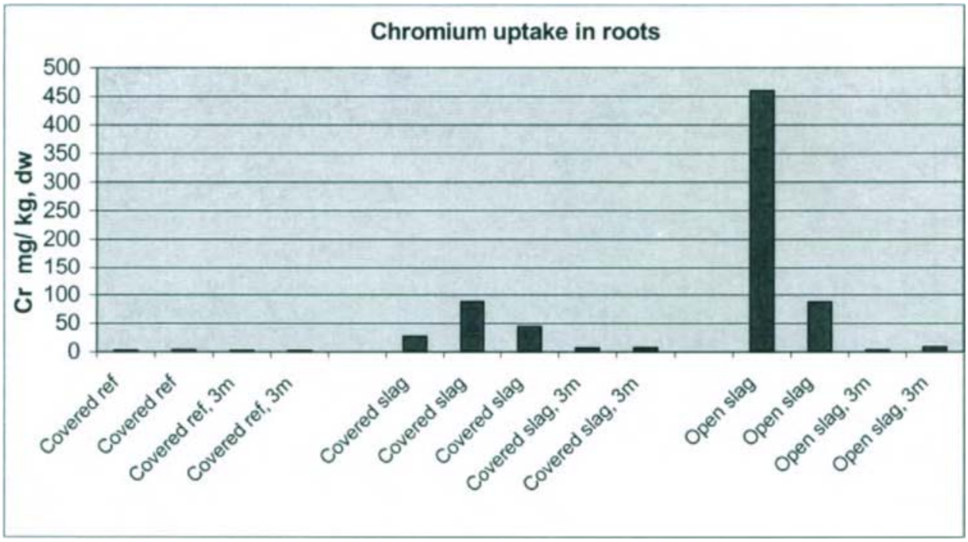

Figure 2. Chromium uptake by roots of dandelion. Samples composed of roots from ten plants each. Samples collected in the slag or macadam at the roads or as reference samples 3 m from the road.

Table 3.
The content of some inorganic elements in roots from dandelion plants (*Taraxacum officinale*) expressed as mg/kg dry weight.

Site	Material	As	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sn	V	W	Zn
Covered site, Macadam	Macadam	0.2	0.66	0.8	2.5	20	0.2	2.7	4.3	0.05	2.5	0.24	59
	Macadam	0.4	0.93	1.4	3.6	28	0.3	4.3	7	0.03	4.7	0.3	181
	Reference, 3m	0.2	1	1.1	2.3	18	0.3	1.9	2	0.02	2.8	0.22	57
	Reference, 3m	0.1	0.51	0.6	1.9	15	0.2	1.2	1.4	0.03	1.4	0.11	40
Covered site, slag	Slag	0.1	0.35	0.8	26.9	22	0.8	3.4	0.9	0.27	2.3	0.13	30
	Slag	0.2	1.17	0.8	88.1	36	0.8	5.6	1.3	0.04	2.7	0.2	25
	Slag	0.1	0.95	0.5	44.7	23	0.7	2.1	0.7	0.03	1.4	0.19	25
	Reference, 3m	0.1	1.13	0.5	6.6	19	1.7	2.7	2.6	0.04	1.5	0.12	83
	Reference, 3m	0.4	1.42	1.5	7.3	28	0.5	6.3	2.7	0.06	5.8	0.19	61
Uncovered site	Slag	3.6	0.47	1.7	460	45	10.2	7.1	19.1	0.75	8.3	1.3	78
	Slag	0.3	0.24	0.6	87.4	20	3.7	3.1	5.9	0.05	2.3	0.15	35
	Reference, 3m	0.3	1.67	0.3	3.7	18	0.6	5.2	5.8	0.04	2.3	0.05	174
	Reference, 3m	0.3	0.26	0.7	8.1	13	3.5	1.4	6.1	0.04	4.2	0.18	51

3.3. Groundwater chemistry

The groundwater samples (unfiltered and filtered) were analysed for 48 elements. Twelve elements were evaluated and the results are presented in Table 4.

Table 4 Concentrations in ground water on three sampling occasions expressed in µg/l. Untreated and filtered samples.

	Filtration	pH	Eh mV	As	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sb	Se	V	Zn
Detection limit				0.1	0.01	0.1	0.1	0.1	0.1	1	0.1	0.01	0.1	0.1	0.1	0.1
Covered site	1 m distance															
18/06/99		5.67	308	7.3	1.19	37.8	237	285	1680	3	477	60.9	0.8	22.5	173	1390
18/06/99	Filtered			2.2	0.18	4.4	13.5	18.6	265	3	42.6	5.55	0.6	4.4	18.9	103
14/07/99		5.84	350	0.8	0.06	1	2.4	9.1	33	<1	4.3	0.73	0.1	1.4	0.7	26
14/07/99	Filtered			0.7	0.07	0.9	1.7	7.7	28	<1	3.7	0.68	0.1	1.3	0.8	34.8
12/08/99		4.99	342	0.6	0.03	0.8	1.4	6.6	18	<1	1.9	0.82	0.2	1.2	0.7	16.9
12/08/99	Filtered			0.8	0.07	0.9	2	6.8	25	<1	2.3	2.23	0.1	1.4	0.8	36.7
Covered site	4 m distance															
18/06/99		5.41	311	4.9	0.72	21.9	118	89.9	898	3	204	38.3	0.6	11.4	88.6	258
18/06/99	Filtered			1	0.12	5.8	7.8	3.7	296	3	75.4	0.8	0.4	3.8	3.1	60.8
14/07/99		5.51	395	0.5	0.15	2.8	1	8.1	74	<1	13.2	0.9	<0.1	1	0.9	43.1
14/07/99	Filtered			0.6	0.12	2.7	1.4	5.5	63	<1	11.9	2.93	<0.1	1	0.4	38.5
12/08/99		4.74	320	0.9	0.18	4.7	8.2	25.9	162	<1	11.2	6.47	0.2	1.9	11.8	71.2
12/08/99	Filtered			0.5	0.11	2.4	1.3	6.5	46	<1	6.3	0.44	0.1	1	0.4	60.2
Uncovered site	Slag															
18/06/99		6.1	209	2.7	0.03	1.2	12.3	3.2	473	<1	9.5	2.31	<0.1	11.8	8.1	22
18/06/99	Filtered			1.8	0.04	0.8	1.6	0.9	441	<1	8	0.15	<0.1	10.1	2.6	8.6
14/07/99		6.2	117	3.4	0.04	2.4	10.9	3.1	1100	1	15.7	1.35	0.1	14.3	6.7	37.5
14/07/99	Filtered			3.6	0.01	1.8	1.5	1.3	1090	1	13.2	0.86	<0.1	15.1	3	15.8
12/08/99		5.98	174	4.5	0.14	3.4	22.5	8.7	1600	<1	21.1	5.13	0.2	17.4	11.6	70.4
12/08/99	Filtered			4.1	0.02	2.3	2.1	1.6	1490	<1	16.8	0.57	0.1	17.1	4	35
Uncovered site	Reference															
18/06/99		5.97	271	4.1	0.34	8	24.1	87.7	310	<1	17.4	43.1	0.3	11.4	105	2100
18/06/99	Filtered			1.9	0.12	1.1	10.8	9.2	98	<1	5.6	4.33	0.3	4.6	26	18.5
14/07/99		6.45	268	3.2	0.14	14.1	55.6	70.9	552	2	30.2	29.6	0.1	7.6	112	144
14/07/99	Filtered			2	0.05	1.7	16.5	12	136	<1	8.8	35.2	0.3	4.3	38.8	31.8
12/08/99		5.45	264	3.2	0.1	2.9	26.3	20	171	2	17.4	9.17	0.3	5.5	44.9	67.3
12/08/99	Filtered			2.8	0.08	1.1	22.4	11.6	110	2	13.7	4.44	0.3	4.6	35.3	44.2

The groundwater levels were relatively stable over the measurement period. The pH values were on the acid side, which is common in the region (Lång 1995; Aastrup 1999). A redox potential lower than oxidised conditions was measured in all samples. However, consistently lower redox potential was measured in the samples from below the uncovered slag, see Figure 3.

The first sampling occasion at the covered site (at a distance of 1 m and 4 m from the road) was 48 hours after the installation of the pipes and the samples contained high amounts of suspended particles. These two samples showed a clearly higher content of most elements. They were not considered to be representative and were subsequently not included in the evaluation.

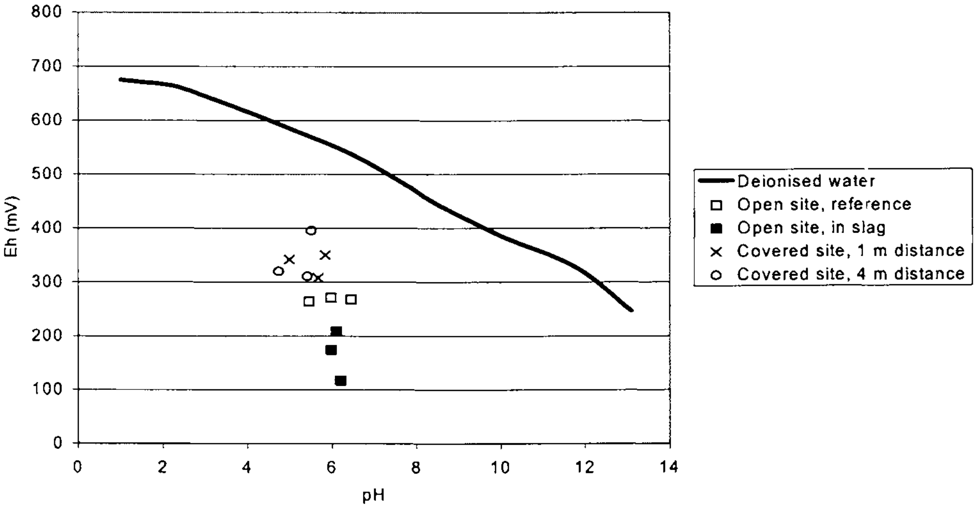

Figure 3. Redox potential and pH in the groundwater at the asphalt-covered site and at the open site.

Filtering of the samples showed that there was a clear particle-bound transport of Cr and Cu and also of Mn, Ni, V and Zn at the covered site. There is a general tendency towards a greater reduction by filtration at initially high Cr-concentrations and at the open site there is also a tendency towards greater Cr-reduction from the groundwater under the slag compared with the 3 m- reference, see Figure 4 and Figure 5. At the open site the filtering resulted in a 15 to 90 % reduction in the Cr-concentration. The results indicated that a large part of the chromium was in trivalent form, Cr(III), associated with fine particles from the slag or in the form of non-soluble hydroxide complexes.

On the whole the chemical composition of the groundwater directly under the slag and the groundwater some metres away were very similar. However, the high Pb-concentrations at the uncovered 4 m reference site were notable, as were the relatively high Hg-concentrations.

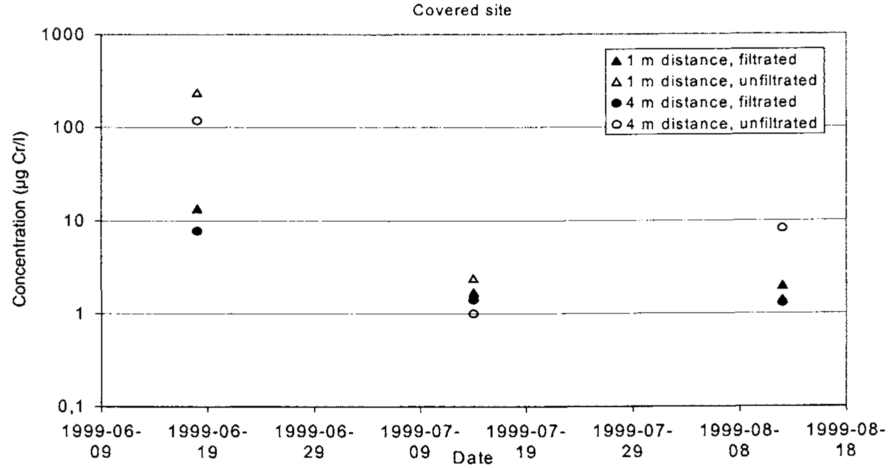

Figure 4. Chromium concentrations in groundwater samples from the asphalt-covered site.

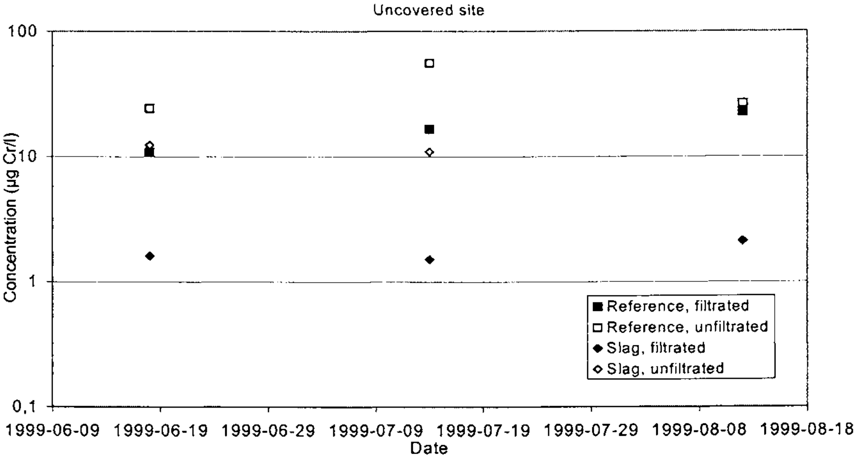

Figure 5. Chromium concentrations in groundwater samples from the open site.

4. DISCUSSION

Investigations of metal uptake by plants are of course totally dependent on undisturbed and uncontaminated samples. Despite careful washing it is possible that small particles from the substrate might be left on the roots. For the samples in this investigation at least five grains, 1mm^3 in size, were required to give chromium concentrations of around 100 mg/kg, dw. We considered such a contamination to be highly unlikely. It was also clear that no other elements, apart from Cr, showed correspondingly increased levels – there was no “fingerprint” of the slag in the root analysis. A "fingerprint" of the slag with a Cr-concentration of about 450 mg/kg should include, for example, 11 mg/kg of W, 9 mg/kg of Ni and 1.04 mg/kg of Sn. Moreover, it has been shown that HNO_3 acid has a relatively weak ability to release chromium from slag products (Fällman & Johansson 1996). Tests with 4 h boiling of slag in 1:10 HNO_3 acid resulted in a very limited release of chromium. It can also be added that a large number of plants are known to accumulate metals from the substrate. So-called “hyperaccumulator plants” may accumulate 1,000 ppm chromium in the leaves from a Cr-rich substrate (Cornish et al. 1995). At this point we must accept that the results presented reflect the true uptake by the plants.

The chromium uptake in plants is controlled mainly by the soluble Cr(VI) content, although the uptake and translocation in the plant is very complicated (Kimbrough et al. 1999). The occurrence of hexavalent or trivalent chromium in groundwater is dependent on both pH and redox potential. The hexavalent chromium is a strong oxidising agent that reacts with organic matter and is reduced to trivalent chromium. The pH - redox potential relationship in the groundwater samples indicated a predominance of the triavalent form of chromium, with relatively low mobility (Brookins 1988). The chromium in the filtered samples was interpreted as mainly hexavalent chromium and was consequently low, in the region of 1-2 µg/l. An exception was the reference pipe at the uncovered site, where concentrations were in the order of one magnitude higher.

It was obvious that Cr-uptake in the plants occurred despite the general conditions of low Cr-solubility. Cr-reduction might come some way to explaining the Cr-uptake. It has been shown that the presence of organically degradable material, sulphides and/or Fe(II) in Cr(VI)-contaminated water may lead to a reduction of Cr(VI) to insoluble Cr(III) oxides (Fendorf 1995). Hypothetically, Cr(VI) may have leached from the slag and been partly adsorbed by the roots of the plants. However, the relatively low concentration of Cr in the narrow, underlying groundwater may have been a result of the reduction of Cr(VI) by for example Fe(II). At the uncovered site a hydrogen sulphide odour was detected, indicating bacterial degradation activity. Microbial degradation of the natural organic matter may produce Fe(II) within the range of the measured redox levels, which in turn may have reduced Cr(VI). However, the Fe content of the groundwater was unknown, though there was organic material present and in some cases hydrogen sulphide.

The toxicity of chromium may vary a great deal between different biota and different conditions. Cr(VI) is known to be toxic to plants, animals and humans, in contrast to Cr(III) which is concidered to be relatively nontoxic (e.g. Bader et al.1999; Veenstra et al. 1999; Kimbrough et al. 1999). Several authors have reported damage to roots and leaves at total chromium contents between 1 and 10 ppm (Kabata-Pendias & Pendias 1992). The concentration of metals is usually much higher in the root than in the leaves and shoots. One study did show that the chromium uptake in tomato roots is four times higher than in the tomato tops (20 resp. 5 ppm), at a chromium content of 150 ppm in the ground (Kabata-Pendias & Pendias 1992). If, as in the case of tomatoes, we assume that the Cr-concentrations in the dandelion roots were four times higher than in the plant above the ground, this will give approximately 10-20 ppm in the leaves. It can thus not be excluded that the chromium uptake has a damaging effect on plants with roots directly in the slag. On the other hand, does the plant uptake lead to a transformation of the more environmentally-damaging Cr(VI)-form to the more stable and less problematic Cr(III)-form (Chaney et al. 1997). The risk of bioaccumulation by birds and other animals eating plants along the roads has not been studied but there is generally regarded to be little bioconcentration or biomagnification of Cr(VI) in the environment (Kimbrough et al. 1999).

From the chemical analysis of the two soil horizons under the slag it was concluded that no extensive downward migration of fine particles occurred from the slag. No chemical influence from the slag could be seen in the underlying soil.

Compared to Swedish criteria for groundwater quality all the elements show none to small influence from source-spot, except for Pb at the open site, which indicated a heavy influence (NV 4918). This should be considered together with the high Pb-uptake that was found in reference plants from this site. The Hg-concentrations in several samples, both filtered and unfiltered, were between 1 - 3 µg/l, which - according to target values based on health criteria for drinking water - represents moderate contamination, (NV 4918). The majority of the samples from the slag sites had Cr-concentrations well below the target values for drinking water (SLV, FS 1993:35). The Cr-concentrations in the groundwater were in the same range as was obtained by leaching at L/S 2 of the ferrochrome slag (Larsson 1995).

Compared to what is known about the regional groundwater quality the concentrations in filtered samples of Cd, Cu and As were low at the investigated sites, whereas the concentration of Mn was high at the open site and low at the covered site. The concentrations of Zn were slightly high in all samples (Wikner et al. 1991; Engqvist et al. 1995; NV 4918; Aastrup 1999).

Soil analysis as well as groundwater analysis showed no significant contamination from the slag. The high levels of Cr in one of the root samples from the open site was associated with high levels of e.g. As, Mo and Pb. High levels of Pb was also found in the groundwater at this site. This is notable considering the fact that the slag has very low concentrations of these elements (see Tab. 1). The influence from other sources can not be excluded and might be linked to the fact that the surrounding terrain is used as a shooting range.

Our conclusion is that the ferrochrome slag constructions could be regarded as a geochemical anomaly in the regional environment. Geochemical Cr-anomaly can also be found under natural conditions, with Cr-rich bedrock for example, in ultramafic rocks with a Cr-content of around 1,000 to 3,000 mg/kg (Jensen & Bateman 1979). The long-term environmental impact of the ferrochrome slag should be compared to that of Cr-rich bedrock. However, the knowledge of the environmental impact of the Cr-uptake by plants is very limited. The presence of Cr(VI) is related to complex bio- /geochemical processes involving Fe, Mn organic matter and sulphides. Risk assessment of the environmental impact of Cr must be very site-specific. There is a need for further research on the spread and bio-accumulation of chromium from uptake by roots and plants in Cr-rich substrate.

7. CONCLUSIONS

We have summarised our conclusions as follows:

* There was a low migration of fine particles from the slag to the underlying soil.

* The leaching from the ferrochrome slag to the groundwater was low for all the elements analysed.

* The concentration of Cr in the groundwater corresponds to the L/S 2 leaching. The leaching seems to occur quite rapidly and can be expected to give a steady state within a few years.

* There seems to be a significant uptake of Cr by plants growing with their roots in the ferrochrome slag, although further investigations are needed to verify this.

* The uptake by plants may be the most important mechanism for spreading elements from the slag to the environment.

* Investigation of plant uptake would be an important complement to laboratory leaching tests of alternative materials.

8. ACKNOWLEDGEMENT

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Mineralogical, hydraulic and mechanical characterisation of solidified and stabilised MSWI fly ash
Contribution of blast furnace slag

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Ashes produced from the Incineration of Municipal Solid Wastes (MSWI fly ashes) require to be treated before being landfilled in a waste disposal site. One treatment method commonly used prior to landfilling is the solidification/stabilisation process using a hydraulic binder. In this study, ground granulated blast furnace slag was used. This binder is well adapted to the solidification and stabilisation of heavy metals. It also offers good durability with regards to chlorides. MSWI ash studied in this paper are derived from an incineration plant which uses dry flue gas treatment.

First, these MSWI ashes are characterised (unhydrated material, reactivity and mechanical properties of hydrated material).

Then, «ash-slag-water» mixtures have been studied to model the properties of fresh and hardened materials. It has been shown that blast furnace slag participated in the solidification/stabilisation of MSWI ashes by: performing the mechanical strength, the durability and the stabilisation of the material.

Then it is shown that an addition of pozzolanic or hydraulic materials performs the solidification and stabilisation properties.

1. INTRODUCTION

The rising production of MSW (Municipal Solid Waste) in France has required increasing and improving methodology for their treatment. The Incineration of these wastes is considered only as an intermediate waste processing technology: ashes derived from the incineration of MSW (MSWI fly ash) still require further treatment before they can be landfilled in hazardous waste disposal sites. Indeed these residues are powdery materials that contain some toxic elements, in particular heavy metals. One treatment method commonly used today to solidify and to stabilise the MSWI fly ash uses some hydraulic binders.

Study of these materials (MSWI fly ash) before their solidification/stabilisation is often limited, in literature, to the determination of the chemical composition and the mineralogical phases. Only a few authors go further into the analysis of the MSWI fly ash by a study of its potential hydraulic activity and the study of chlorinated residues recovered from the dry flue gas process is little developed. Indeed major part of residues studied are ashes recovered from a wet process. The MSWI fly ashes studied here are produced from a dry flue gas treatment. *This work first proposes a tentative characterisation of the MSWI fly ash material by the study of its mineralogical, hydraulic and mechanical properties.* A better knowledge of this material will later permit an estimate of the role and the efficiency of the binder used in solidification/stabilisation processes, in our case the blast furnace slag.

It appeared useful to initially study the anhydrous phases of the MSWI fly ash material, by means of chemical and microstructural analyses.

Having noted during exploratory tests, that these anhydrous phases, in presence of water, presented a phenomenon of setting and hardening, we have characterised the rheology of the fresh material, “MSWI fly ash + water”, after having defined one procedure for the realisation and the placing of mixes. In particular, we studied the influence of the water temperature on this rheology. We characterised thereafter the efficiency of the hardened material *solidification and stabilisation.* In order to complement this analysis of the MSWI fly ash, we made a microstructural study to specify the hydrated phases and their evolution in time.

In a second phase, this work presents the influence of slag addition on properties of the fresh and hardened material previously studied . *After exploratory test results to determine the use of slag, mixes of slag, MSWI fly ash, water and admixtures were completed. The role of the slag content is considered in the process of hydration, solidification and stabilisation of the mix. Its involvement to the improvement of durability properties was also studied. A microstructural analysis of mixes complements this study.*

Finally, it is proposed an extension of the solidification/stabilisation process by the use of hydraulic or pozzolanic additions.

2. CHARACTERISATION OF THE MSWI FLY ASH

2.1. Mineralogical characterisation of anhydrous material

The XRD and DTA analyses identified the following mineral phase : $CaClOH$, $Ca(OH)_2$, $CaSO_4$, $NaCl$, KCl, SiO_2, $CaCO_3$. Some complementary chemical analyses completed this analysis and showed the presence of CaO, Al_2O_3 and many heavy metals. The most frequent and more leachable heavy metals in the MSWI fly ash are Pb, Zn, Ba and Sr.

The MSWI fly ash contains a great amount of potentially reactive compounds (in presence of water and others constituents of the MSWI fly ash or by air carbonation), in particular $Ca(OH)_2$ and $CaClOH$. The presence of these compounds persuaded us to study the reactivity of this material, to characterise its behaviour when it is mixed to water.

2.2. Hydraulic properties of the MSWI fly ash, mechanical behaviour and stabilisation of the hardened material

The MSWI fly ash is reactive when mixed with water and presents a setting whose kinetics depends on the water temperature (cf table 1).

The "hydration" of the MSWI fly ash produced an important exothermic reaction of solubilisation and a swelling (cf table 1) due to a production of H_2, the result of a reaction between the lime and residues of metallic aluminium. When the material hardens, the swelling stops, but the potentiality of the MSWI ash to develop a swelling reaction remains.

This swelling reaction was stopped by the addition of a waterproof admixture. The increase of the water temperature has a great delaying effect on the setting of the material and liquefies it, the swelling is increased physically by delay of the setting time and chemically by change of solubilities.

Table 1
Influence of the temperature of the mixing water on the fresh material properties (Water/MSWI ash = 0.5)

Water temperature (°C)	Initial setting time (min.)	Swelling (%)
4.5	20	4
10	17	2
20	49	7
48	90	9
50	73	7.5
65	105	15

The MSWI fly ash is therefore a significantly reactive material with water.

The MSWI fly ash material presents a hardening phenomenon (see fig. 1), but this process is not really hydraulic. Indeed it has been observed that the crystals formed are not tolerant to water in the short and medium term. Additionally, the mechanical strength doesn't progress in time.

In spite of this, the "hydration " of the MSWI ash brings about a stabilisation of the heavy metal leaching and the ageing of the material reinforces this stabilisation. However, the soluble elements (FS, Cl, Ca), are not combined by the setting of the MSWI fly ash alone.

Therefore, the MSWI fly ash material produces solidification but it is absolutely necessary to use an hydraulic binder to ensure good stabilisation.

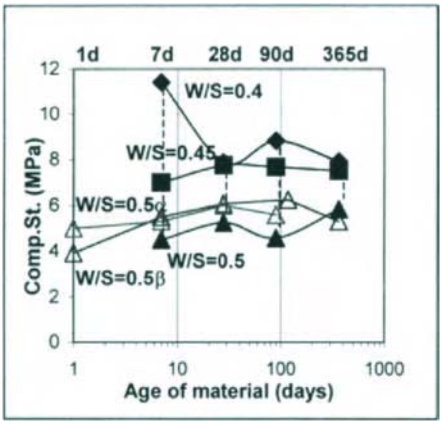

Figure 1. Development of compressive strength (Comp.St.) with time relating to Water/Solid ratio.

Finally, the solidification doesn't prove to be enough since thermal and hydraulic particular conditions are strongly harmful to the durability of the material (to see & 2.3). It is therefore necessary to study the solidification of the MSWI fly ash on the other criteria basis than those fixed by the French standard X 31-212.

Moreover, the mechanical strength development versus time of the solidified material does not suggest good long term behaviour (cf. fig. 1).

The need to use a hydraulic binder is confirmed by a non-enduring solidification.

2.3. Understanding of phenomena

Microstructural analyses and studies on artificial material permitted us to advance these explanations :

- The solubility of MSWI fly ash is a decreasing function of the temperature (because $Ca(OH)_2$ and CaClOH), which explains the influence of the temperature on the kinetic of setting.
- CaClOH is responsible for the exothermic behaviour of the MSWI fly ash.
- The setting of the MSWI fly ash and the short-term strengths of the MSWI fly ash are caused by the hydration of CaClOH in presence of a basic pH or lime. The formed material is a calcium chloride hydrate, soluble to water (increasing solubility with the temperature). It is this behaviour that is responsible of the physical destruction in water in the short and medium term and of the negative effect of temperature cycles on strengths of the hardened material . This increasing solubility according to the temperature is also responsible of the fast setting of the MSWI ash. The short setting time is bound to the fact that it is difficult to discern phases of hydration and growth and one comes closer more of the behaviour of a chemical compound that precipites (CaClOH) than of a hydraulic compound that hydrates itself.
- The "hydration " of MSWI ash leads to the formation of a calcium chloride and a calcium chloride aluminate . Its " hardening " seems to be accompanied by a carbonation of the material and by the appearance of a derivative shape of ettringite (chloro-ettringite). In addition, the consumption of lime during the ageing of the material and the transformation of the calcium chloride hydroxide CaClOH are demonstrated.
- However, we didn't succeed in identifying where in the hydrated phases the heavy metals were stabilised.

3. CHARACTERISATION OF THE MSWI FLY ASH, SOLIDIFIED AND STABILISED BY BLAST FURNACE SLAG

3.1. Choice of the slag

Blast furnace slag is an appropriate binder for solidification/stabilisation of MSWI fly ash, because it presents several modes of activation, and, the constituents of the MSWI fly ash make part of the slag's potential activators. It is also well known that the blast furnace slag presents a slower hydration with a low heat of hydration. Moreover, the hardened slag presents a better durability to aggressive chemicals and a lower permeability (lesser diffusion) than the Portland cement.

We compared the efficiency of blast furnace slag of different finenesses:

- slag 1: d98=100μm;

- slag 2: d98=28µm;
- slag 3: d98 <6µm

Our criteria of comparison are the mechanical strengths at different ages and the behaviour of materials when they are immersed in water. The analysis of results lead us to choose the slag n°2 to achieve the process of solidification/stabilisation and to survey the influence of slag rate on criteria of solidification and stabilisation after the material processing.

3.2. Influence of the slag content on the solidification/stabilisation of the MSWI fly ash

Choice of mixes

The aim is to formulate a composition " MSWI fly ash + water + slag + admixtures ".

We kept three parameters of formulation: MSWI ash ratio in the solid phase (MSWI fly ash + slag), water ratio and water temperature. The waterproof admixture, necessary to inhibit the reaction of swelling observed on the "MSWI fly ash + water" mixture is added to a rate of 1% in relation to the weight of MSWI ash.

We modelled the material behaviour (its properties) according to parameters of formulation for the tests corresponding to normative, technical and economical criteria. Hence, we will be able to clearly identify the slag's participation in the process of MSWI fly ash solidification and stabilisation.

We used the statistical design of experiments methodology to determine these mathematical models. This method permits you to organise some parametric analyses in order to minimise the number of experiments to obtain all the data to determine the effect of parameters and their interactions. Compared with a usual empirical methodology, the gain tackles in won time and in rigor in the exploitation of results.

The ranges of variation of the 3 factors of formulation are given in the table 2.

Table 2
Variation ranges of factors

	MSWI fly ash / Slag x_1	Water / (MSWI ash+slag) x_2	Water temperature (°C) x_3
Lower value (-1)	50/50	0.4	5
Superior value (+1)	100/0	0.6	45

The statistical design of experiments lead us to achieve sixteen experiments to cover the whole experimental domain and to determine the mathematical models for the following tests:

- measures on unhardened material : workability, setting time, swelling,...
- mechanical tests on hardened material (to different ages)
- study of the stabilisation on hardened material: measure of the conductivity of the filtered liquid obtained from the hardened material immersion to several ages, leaching test...

Experimental results - mathematical models determination

We present in this paper the mathematical models obtained for some of modelised tests; x_1, x_2 and x_3 are used in coded values (brings in -1 and 1) defined table 2.

Compressive strength (28 days) :

$Comp.St._{28} = 12.9 - 3.8x_1 - 8.4x_2 + 1.1x_3 - 0.5x_1^2 + 0.8x_2^2 + 0.5x_3^2 + 2.3x_1x_2 - 1.5x_1x_3 - 0.5x_2x_3 + 1.9x_1x_2x_3$

Conductivity of filtered liquid obtained from the immersion of an aged sample (28 days) :

$Cd_{28} = 7.96 + 5.57x_1 + 0.27x_2 - 0.39x_3 + 0.25x_1^2 - 0.50x_2^2 + 0.02x_3^2 + 0.30x_1x_2 - 0.40x_1x_3 + 0.06x_2x_3 + 0.08x_1x_2x_3$

Measure of the soluble content of the leachate - aged samples of 60 days:

$Sol.Cont. = 4.4 + 4.5x_1 - 0.2x_2 - 0.9x_3 + 1.1x_1^2 + 0.5x_2^2 - 0.1x_3^2 - 0.1x_1x_2 - 0.5x_1x_3 + 0.5x_2x_3 + 0.5x_1x_2x_3$

Analysis of models – study of the slag's influence

After validation and analysis of these models (thanks to the analysis of the response surfaces) and others not presented here, we arrived at the following conclusions:

- Increasing slag content improves the workability of the **fresh material** and prolongs the initial setting time (interactions exist between the initial setting time and the factors temperature of water and water/solid ratio).
- The effect of slag content on the **mechanical strengths** is a function of the age of the material, of water/solid ratio and of its temperature. It should be noted that a high slag content is prejudicial to the mechanical strengths of a 24 hour old material. In this time, the slag is not sufficiently hydrated. At later ages a high slag content develops a good mechanical strength with higher gains of strength with time.
- A high slag content always allows **stabilisation** of the material to improve (analysis of the leaching) and to decrease the conductivity of the leachate, but this effect is influenced by values taken by the other factors. Slag's contribution doesn't have a simple effect of dilution on the stabilisation of the material, but it participates efficiently in the chemical stabilisation of the soluble products. This action is more and more efficient as the material hardens.

3.3. Involvement of the slag in the improvement of the durability of the material

After the analysis of the mixes "MSWI ash + water + slag + waterproof admixture", an optimised composition* has been determined and worked up in order firstly to validate the accurateness of the models of behaviour and secondly to control the acceptability of the material put in landfill towards the actual standards.

The optimised composition found is the following:
36.5% of slag, 63.5% of MSWI fly ash, temperature of the water: 30°C, content in waterproof admixture: 1% by weight of MSWI fly ash.

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* Calculated thanks to a multi-criteria optimisation.

We submitted solidified materials of different compositions (optimised one and others) to the following cure conditions:

- 10 thermal day/night cycles between 50°C and -25°C.
- immersions for 96 hours in neutral or aggressive baths.

After these cycles and immersions, mechanical strength tests have been completed on samples. We compare these whole results to those obtained with samples having undergone no cycle nor immersion (*reference*).

Details of compositions :

- Composition 1: 36.5% slag /63.5% MSWI ash => Optimised composition
- Composition 2: 100% MSWI ash => MSWI composition
- Composition 3: 90% slag / 10% lime => Slag composition

Table 3

Compressive strength of materials (MPa) under special hydrothermal conditions

Temperature Cycle	C1	C2	C3
Alternating (50°C-20°C-25°C-20°C)	18.5	2.3	19
hot 50°C-20°C)	20	7	17
cold (-25°C-20°C)	21	12.5	15.5
reference	20	14.5	15
Immersion Cycle	**C1**	**C2**	**C3**
pH 7	22	2	17.5
pH 4.5	19	2.2	16
pH 12.5	22.2	2	16
reference	21.5	13.2	15

Thus, the addition of blast furnace slag gives a guarantee of durability of the solidified and stabilised material since it is not affected by the thermal cycles or the prolonged immersions contrary to the MSWI composition which is highly affected.

3.4. Modifications of the material microstructure

The MSWI ash solidification in the "MSWI ash + water" mixture is achieved mainly by the formation of a chloroettringite and in less quantity of ettringite and calcium chloroaluminate.

We showed by DTA and XRD analysis that slag's presence produced a reduction of this chloroettringite to the benefit of the ettringite and the chloroaluminate. In addition, the presence of CSH was also noted. We also observed to the MEB that the internal porosity of the material is decreased by the increase of slag content.

4. IMPROVEMENT OF PROPERTIES OF THE HARDENED MATERIAL BY THE ADDITION OF HYDRAULIC AND POZZOLANIC CONSTITUENTS

With the aim of decreasing the cost of the process and improving the stabilisation of the optimised composition material, we substituted a slag's fraction (1/4) by different additions.We recall that the optimised composition is the following:
36.5% of slag, 63.5% of MSWI ash, temperature of the water: 30°C, content in waterproof admixture: 1% in weight of MSWI ash. The substituted material represents 9% of the solid phase (27.5% of slag).

We noted that silica-alumina ashes (pulverised coal ash) and sulfocalcic ash (fluidizided bed combustion plant) improved the solidification of the material, and, silica-alumina ash and métakaolinite improve the stabilisation.

5. CONCLUSION

MSWI fly ash studied here, derived from a dry flue gas treatment, is constituted mainly of mineral phases CaClOH, $Ca(OH)_2$, $CaSO_4$, Al_2O_3 and SiO_2.It also contains amounts of heavy metals (lead, zinc,...).

The MSWI fly ash is a reactive material, and presents a setting when it is mixed with water whose kinetics is a function of the water temperature and a hardening accompanied by a partial stabilisation of the heavy metals. However the durability of the "MSWI fly ash + water" hardened material is not satisfactory and its stabilisation is not sufficient.

After experimental tests, we chose a fine powdered vitrified blast furnace slag in order to solidify and to stabilise the MSWI fly ash. It has been shown that the slag's involvement in the process of solidification/stabilisation of the MSWI ash affects mechanical strengths and durability by material improvement, on the physical packaging by formation of a strong matrix, and on an efficient involvement in the chemical process of stabilisation. A minimum slag content of 30% is necessary to assure a good solidification/stabilisation and simultaneously a sufficient durability . We have to note also that water/solid ratio influences the slag's efficiency.

It has also been shown that an addition of thermal plant fly ashes (PFA & FBCA) allowed an improvement to some properties of the hardened material.

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Lead, zinc and chromium (III) and (VI) speciation in hydrated cement phases.

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Cement contains trace amounts of heavy metals of various origins. The main source is due to heavy metals naturally present in some of the raw materials used for clinker manufacture. The use of industrial waste as substitutes for fossil fuels may be an other source of heavy metals in cement. During the hydration of cement, anhydrous phases dissolve and species in solution react to form hydrated products. Therefore, the true fixation of the heavy metals is the one inside the precipitated hydrates after the dissolution of anhydrous phases. This work attempts to characterize lead, zinc and chromium (III) and (VI) speciation in hydrated cement phases. The study consists of two steps : (i) examining metal retention from different cement phases by sorption isotherms, (ii) determining metals local structure using two different methods, ^{29}Si and ^{27}Al nuclear magnetic resonance spectroscopy and X-ray absorption spectroscopy (K-edge of Zn, Cr and L^{III}-edge of Pb). This approach reveals that, at least for one of the phases, there are always interactions between hydrated cement phases and metals. The following conclusions have been reached : (i) all metals studied show a strong affinity for hydrated C_4AF "ferrite" phases, (ii) lead and zinc are linked to silicium tetrahedra of C-S-H, (iii) Cr^{III} is structurally incorporated by hydrogarnet phases, (iv) Cr^{VI} show an affinity only for temporary hydrated calcium aluminate phases.

Therefore, this work clearly demonstrates that metals contained in hydrated cement phases have particular retention sites that should be considered when conducting long-term studies of cement leaching and its modelization.

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1. INTRODUCTION

Cement contains trace amounts of heavy metals of various origins. The main source is due to heavy metals naturally present in some of the raw materials used for clinkers manufacture. The use of industrial wastes as substitutes for fossil fuels may be an other source of heavy metals in cement [1].

During the hydration of cement, anhydrous phases dissolve and species in solution react to form hydrated products. Therefore, heavy metals contained in anhydrous phases dissolve too, whatever their localisation (tied up to the crystal structure or present as metal oxide). Therefore, depending on their mode of fixation in the hydrated cement phases, these metal ions may be released later into the environment. Information concerning the exact location of these metal ions is important in gauging the probability of their eventual release. So, it is useful to try to characterise the different sites of the heavy metals in the hydrated cement phases. As cement is a complicated multi-phase product, an interesting approach consists of studying heavy metal retention by each of the hydrated phases. This work attempts to determine speciation of lead, zinc, copper and chromium in hydrated cement phases. The study consists of two steps : (i) examining metal retention from each hydrated cement phase by sorption isotherms, (ii) determining metals local structure using two different methods, nuclear magnetic resonance spectroscopy and X-ray absorption spectroscopy.

The first step is reported to a large extent but only a few results of the second step are presented in order to show the process.

2. EXPERIMENTAL SECTION

2.1.Sorption experiments

To prevent CO_2 contamination, and precipitation of carbonates, all experiments were carried out in a glovebag under nitrogen. Starting materials consisted of (i) a non hydrated tricalcium silicate noted C_3S according the cement nomenclature[1], (ii) C_3S hydrated with lime water (LW) (water/solid ratio of 10) for three weeks on a rotary shaker, centrifuged and dried, noted $[C_3S\text{+LW}]_{21d}$ (iii) a non hydrated tricalcium aluminate C_3A, (iv) C_3A hydrated with lime water (LW) (water/solid ration of 10) for 1 week on a rotary shaker, centrifuged and dried, noted $[C_3A\text{+LW}]_{7d}$ and (v) a calcium aluminoferrite noted C_4AF.

Sorption experiments were performed in lime water to which was added $Pb(NO_3)_2$, $Zn(NO_3)_2{\cdot}6H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$ or $Na_2CrO_4{\cdot}4H_2O$ to obtain initial metal concentrations in the range of $5{\cdot}10^{-4}$ or $1{\cdot}10^{-3}$ to $7{\cdot}10^{-3}$ $\text{mol}{\cdot}\text{l}^{-1}$. For each concentration, a diluted suspension was prepared by placing 3 g of the initial material in 30 g of hydrating fluid in a tube that was then sealed. The suspensions were then equilibrated for 72 hours. The supernatants obtained after centrifugation were analyzed for heavy metals with an AA Hitachy spectrometer Z-8200. The recovered solids were ground to a fine powder and analyzed by X-ray diffractometer using a CoKα radiation at 40 KV and 40 mA.

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[1] Cement nomenclature C : CaO, S : SiO_2, A : Al_2O_3, F : Fe_2O_3, H : H_2O

2.2. Structural investigation

In order to determine metals local structure, two different methods were used : ^{29}Si and ^{27}Al nuclear magnetic resonance spectroscopy and the X-ray absorption spectroscopy (K-edge of Zn, Cr and L^{III}-edge of Pb). In this paper, only a few examples (some ^{29}Si NMR results in the case of lead and some Cr K-edge EXAFS measurements) are discussed ; a more complete presentation of the structural investigation can be found in other publications [2], [3], [4]. Therefore, the description of the methods is summed up briefly. The samples examined by these methods were prepared as already described (sorption experiments) except for the water/solid ratio, which was changed to 36 or 60 in order to increase the metal concentration in samples. Table 1 shows characteristics of the different samples analyzed by ^{29}SiNMR and Cr K-edge X-ray absorption spectroscopy.

2.2.1. ^{29}Si magnetic resonance spectroscopy

NMR spectroscopy is an extremely useful technique for studying the microstructure of solids especially in the case of heterogeneous, multi-phasic materials which are often difficult to analyse by other methods such as X-ray diffraction. Solid state ^{29}Si NMR spectroscopy enable characterisation of silicium sites (coordination, symmetry, distortion...) and has been used by many groups in the study and identification of the different sites present in hydrated C-S-H phases [5][6][7]. By comparing sites distribution of this major element, it is possible to trace a metal impact and to obtain indirectly information on the localisation of the metal. Solid state ^{29}Si NMR spectra were obtained with a Bruker MSL400 spectrometer at 79.49MHz in the "Institut Cienca de Materiales" (Madrid, Spain). Samples were placed into 7 mm MAS rotors and spun at 3kHz. Spectra were obtained from a single pulse excitation (pulse widths 6 μs and 60 s recycle delays). The ^{29}Si chemical shifts were reported in parts per million (ppm) relative to tetramethylsilane. Spectral line fittings were performed with an IGOR software package.

Table 1: Characteristics of the different samples analysed by ^{29}Si NMR and Cr K-edge EXAFS spectroscopy and notation used.

Samples name	Starting material	hydrating fluid	water /solid	contacting time
C_3S	-	-	-	-
$(C_3S+LW)_{72h}$	C_3S	LW	36	72 hours
$[(C_3S+LW)_{21d}+LW]_{72h}$	$(C_3S+LW)_{21d}$	LW	36	72 hours
$(C_3S+LW+Pb)_{72h}$	C_3S	$LW+Pb(NO_3)_2$ at 5.10^{-3} mol.l^{-1}	36	72 hours
$[(C_3S+LW)_{21d}+LW+Pb]_{72h}$	$(C_3S+LW)_{21d}$	$LW+Pb(NO_3)_2$ at 5.10^{-3} mol.l^{-1}	36	72 hours
$(C_3S+LW+Cr^{III})_{28d}$	C_3S	$LW+Cr(NO_3)_2$ at 5.10^{-3} mol.l^{-1}	60	28 days
$[(C_3S+LW)_{21d}+LW+Cr^{III}]_{72h}$	$(C_3S+LW)_{21d}$	$LW+Cr(NO_3)_2$ at 5.10^{-3} mol.l^{-1}	60	72 hours
$(C_3A+LW+Cr^{III})_{7d}$	C_3A	$LW+Cr(NO_3)_2$ at 5.10^{-3} mol.l^{-1}	60	7 days

LW :Lime Water

$(C_3S+LW)_{21d}$ means that C_3S has been hydrated for 21 days with lime water

2.2.2. X-ray absorption spectroscopy

Extended X-ray absorption fine structure (EXAFS) spectroscopy enables the local environment around the studied atom be determined, in this case chromium (named the central atom). Indeed, the number of neighbours and distances between the central atom and neighbour atoms can be determined. Cr K-edge EXAFS measurements were performed at room temperature in the fluorescence mode at the National Synchrotron Light Source (Brookhaven National Laboratory) on beamline X23A2. EXAFS data reduction was accomplished according to a procedure previously described [4]. $k^3\chi(k)$ EXAFS spectra (where k stands for the modulus of the wave vector and is expressed in $Å^{-1}$) were Fourier's transformed from k to R space by using a Kaiser's apodisation window. It gives a pseudo radial distribution function (RDF) uncorrected from phase shift. The contribution of various shells were signalled out by back Fourier transform (including a removal of the kaiser window contribution), from real to k space. These partial EXAFS functions were then least-squares fitted using the electronic parameters extracted from model compounds in which bonding configurations similar to those being investigated are present (Eskolaite Cr_2O_3, Uvarovite $Ca_3Cr_2(SiO_4)_3$).

3. RESULTS

3.1. Sorption experiments

Figure 1, 2 and 3 show respectively the sorption isotherms of Pb(II), Zn(II), Cr (III) and Cr(VI) onto C_3S, $[C_3S+LW]_{21d}$, C_3A, $[C_3A+LW]_{7d}$ and C_4AF.The solubility of metals oxides or hydroxides is also reported [8] .In the case of zinc, the steady phase is $CaZn_2(OH)_6{\cdot}2H_2O$ in conditions of the study (lime water without $C0_2$).

3.1.1. Sorption isotherms of lead

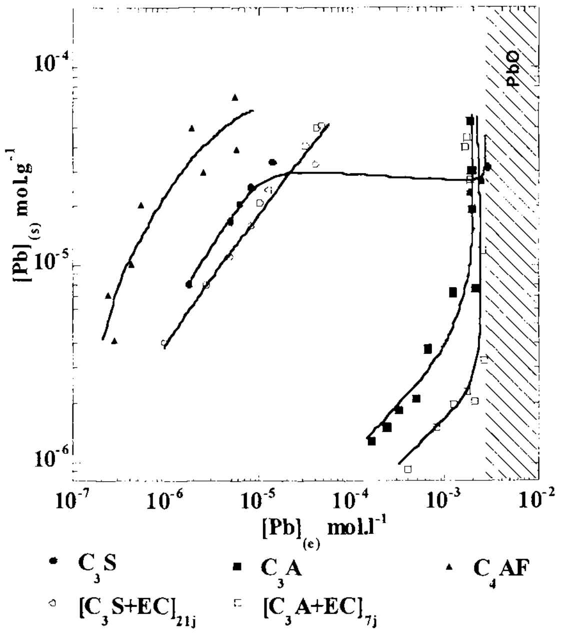
The lead sorption isotherms for C_3S and $[C_3S+LW]_{21d}$ are quite different. For anhydrous tricalcium silicate, the isotherm curve reaches a plateau at $[Pb]_e > 2{\cdot}10^{-5}$ $mol{\cdot}l^{-1}$ but increases rapidly as soon as $[Pb]_e$ reaches the equilibrium concentration of PbO (i.e. $\sim 3{\cdot}10^{-3}$ $mol{\cdot}l^{-1}$). For $[C_3S+LW]_{21d}$ the sorption isotherm increases steadily within the unsaturated region of PbO. For C_3S, the plateau corresponds to a sorbed quantity of Qs $\sim 3{\cdot}10^{-5}$ mol·of lead per gram of initial product. The X-ray diagrams of these plateau samples are characteristic of the non hydrated C_3S material, which means that the hydration of the sample is very limited to these lead contents.

The lead sorption isotherms onto C_3A and $[C_3A+LW]_{7d}$ are very similar. The curves have two parts : the first one corresponds to a very weak lead retention and on the second one, $[Pb]_e$ reaches the lead equilibrium concentration of PbO. On the contrary, the very low concentration of lead in solution shows that this metal is very well retained by C_4AF.

3.1.2. Sorption isotherms of zinc

The zinc isotherms show a relatively high affinity for both C_3S and $[C_3S+LW]_{21d}$. The equilibrium concentration $[Zn]_e$ is below the solubility values of ZnO, $Zn(OH)_2$ and $CaZn_2(OH)_6{\cdot}2H_2O$ to prevent zinc precipitating either in solution or onto solids. The X-ray

Figure 1: Sorption isotherms of Pb(II) onto C_3S, $[C_3S+LW]_{21d}$, C_3A, $[C_3A+LW]_{7d}$ and C_4AF.



diffraction patterns of the solids samples show the presence of the portlandite, indicating that C_3S is at least partially hydrated.

The zinc sorption onto calcium aluminate phases can be separated in two parts. The first one is a calcium hydroxyzincate sursaturated and not steady area, in the second one, $[Zn]_e$ corresponds to the equilibrium concentration of $CaZn_2(OH)_6{\cdot}2H_2O$. Low zinc concentration in solution is reached for C_4AF sorption experiments.

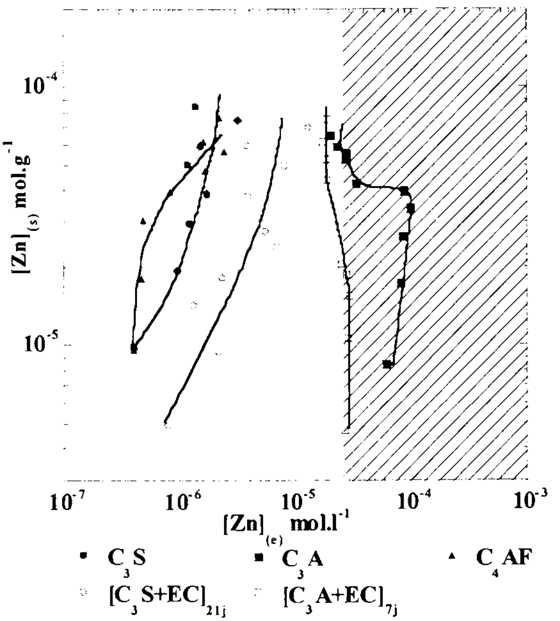
3.1.3. Sorption isotherms of chromium

As chromium is presented in its two oxidation states (Cr^{III} and Cr^{VI}) in cement phases, both are studied. Cr^{III} is sorbed to a great extent whatever the cement phases. The concentration of chromium in solution is very low (about 10^{-6} mol·l^{-1}) and always in unsaturated region. Cr^{VI} is highly soluble in the conditions of the study (high pH). On the one hand, there is a strong retention with calcium aluminate and aluminoferrite, on the other hand, chromium VI shows a weak interaction with calcium silicates whatever their hydration state (C_3S or $[C_3S+LW]_{21d}$).

3.2. Some NMR results

Basically, ^{29}Si NMR spectroscopy enables us to characterize the different silicium sites and more especially the number of bonds between silicates tetrahedra. A widespread notation of silicate sites is Q_n where n stands for the number of bonds with other silicate tetrahedra [9]. Figure 4 displays the relationships between the ^{29}Si NMR spectra shape and crystallographic structure of some cement phases. ^{29}Si NMR spectrum of anhydrous C_3S is only composed of

Figure 2: Sorption isotherms of Zn(II) onto C_3S, $[C_3S+LW]_{21d}$, C_3A, $[C_3A+LW]_{7d}$ and C_4AF.



Q_0 lines from -69 ppm to -75 ppm whereas Q_1 and Q_2 contributions appear in hydrated calcium silicates. Obviously, when lead is added to C_3S and even after 72 hours contact time, no Q_1 or Q_2 contributions arise unlike in the case of the control sample (Figure 5). This lake of tetrahedra connectivity traduces a strong hydration retardation effect of lead.

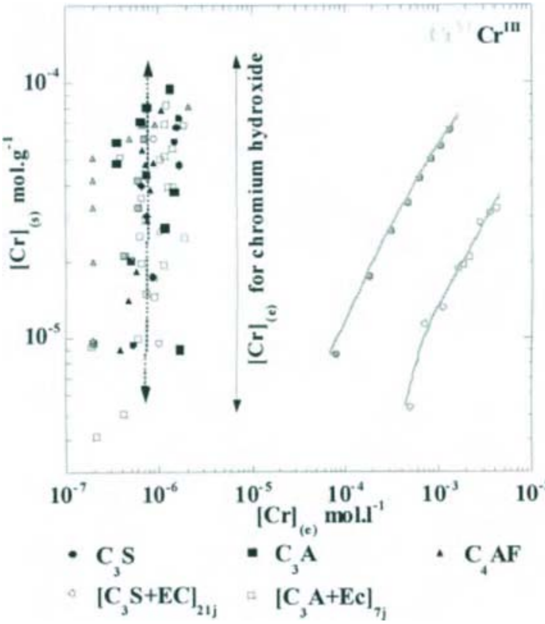
When lead is added after a preliminary hydration stage of the tricalcium silicate $[(C_3S+LW)_{21d}+LW+Pb]_{72h}$, a new line at -86 ppm should be added to the control sample decomposition $[(C_3S+LW)_{21d}+LW]_{72h}$ (figure 5). As discussed in previous work [2], the new line can be attributed to Q_{1Me} (a Q1 site link to metal by one oxygen) site involving Si-O-Pb bonds.

3.3. Some X-ray absorption results

Figure 6 show RDF obtained from Cr K-edge spectrum of samples $[C_3A+LW+Cr^{III}]_{7d}$, $[C_3S+LW+Cr^{III}]_{28d}$ and $[(C_3S+LW)_{28d}+LW+ Cr^{III}]_{72h}$. Structural parameters for Cr - backscatterer contribution derived from EXAFS analysis are listed in table 2. The first peak at 1.6 Å (RDFs distance uncorrected for phase shift function) corresponds to the contribution of oxygen atoms. Analysis parameters obtained for the three samples show the presence of about 6 oxygen atoms at an average distance of 2.01 Å from the central atom. These results imply that chromium is octahedral coordinated and has an oxidation state of III.

In the case of $[C_3A+LW+Cr^{III}]_{7d}$, the second and third peaks (around 3Å uncorrected distances) are assigned to calcium atoms at 3.40 Å and chromium atoms at 3.51 Å. For both

Figure 3: Sorption isotherms of Cr(III) and Cr(VI) onto C_3S, $[C_3S+LW]_{21d}$, C_3A, $[C_3A+LW]_{7d}$ and C_4AF.



$[C_3S+LW+Cr^{III}]_{28d}$ $[(C_3S+LW)_{28d}+LW+Cr^{III}]_{72h}$, the analysis of the second peak indicates the presence of some calcium and silicium atoms at an average distance of 3.3 - 3.5 Å from the central atom (Cr). Distances obtained for $[C_3A+LW+Cr^{III}]_{7d}$ between chromium (central atom) and calcium are quite similar to the distance between aluminium and calcium in calcium aluminate hydrated cubic phase noted C_3AH_6. Therefore, it seems reasonable to suppose that octahedral chromium is able to substitute octahedral aluminium in this hydrogarnet. This assumption is also made by other authors [10]. In the case of calcium silicate, calcium and silicium detected contributions involve the formation of a hydrogarnet in which chromium is in an octahedral site and silicium partially occupied tetrahedral cavity. This kind of silicium site has already been proposed by several authors in the case of hydrogarnet naturally formed in hydrated cement where silicium is present [11].Finally, a hydrogarnet of the type $Ca_3[Al_{1-x}Cr_x(OH)_{6-2y}(SiO_4)_{y/2}]_2$ seems to be formed, whatever the initial cement phase brought into contact with Cr^{III} in lime water.

4. DISCUSSION

4.1. Lead

Results from sorption experiments and ^{29}Si NMR associated with X-ray absorption spectra obtained and discussed in other publications [2] [4], allow us to conclude that lead sorbed onto C_3S surface blocks its hydration. When C_3S is preliminary hydrated, lead is very well

Figure 4: ^{29}Si NMR spectra of C_3S and C_3S hydrated for 3 weeks. Relationships between the ^{29}Si NMR spectra and crystallographic structure of C_3S and C-S-H.

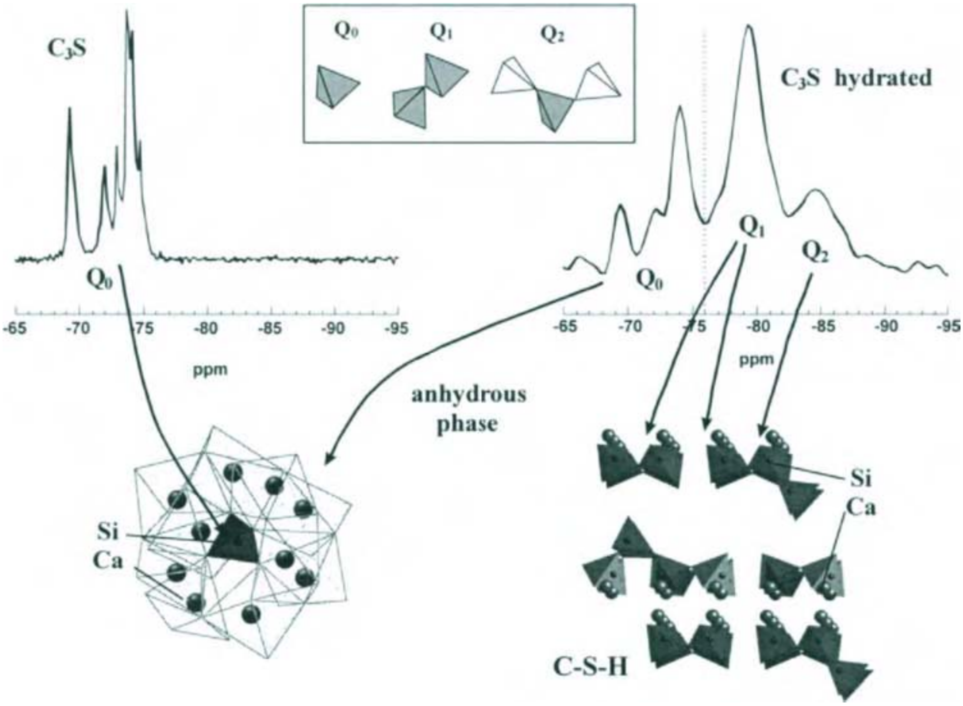
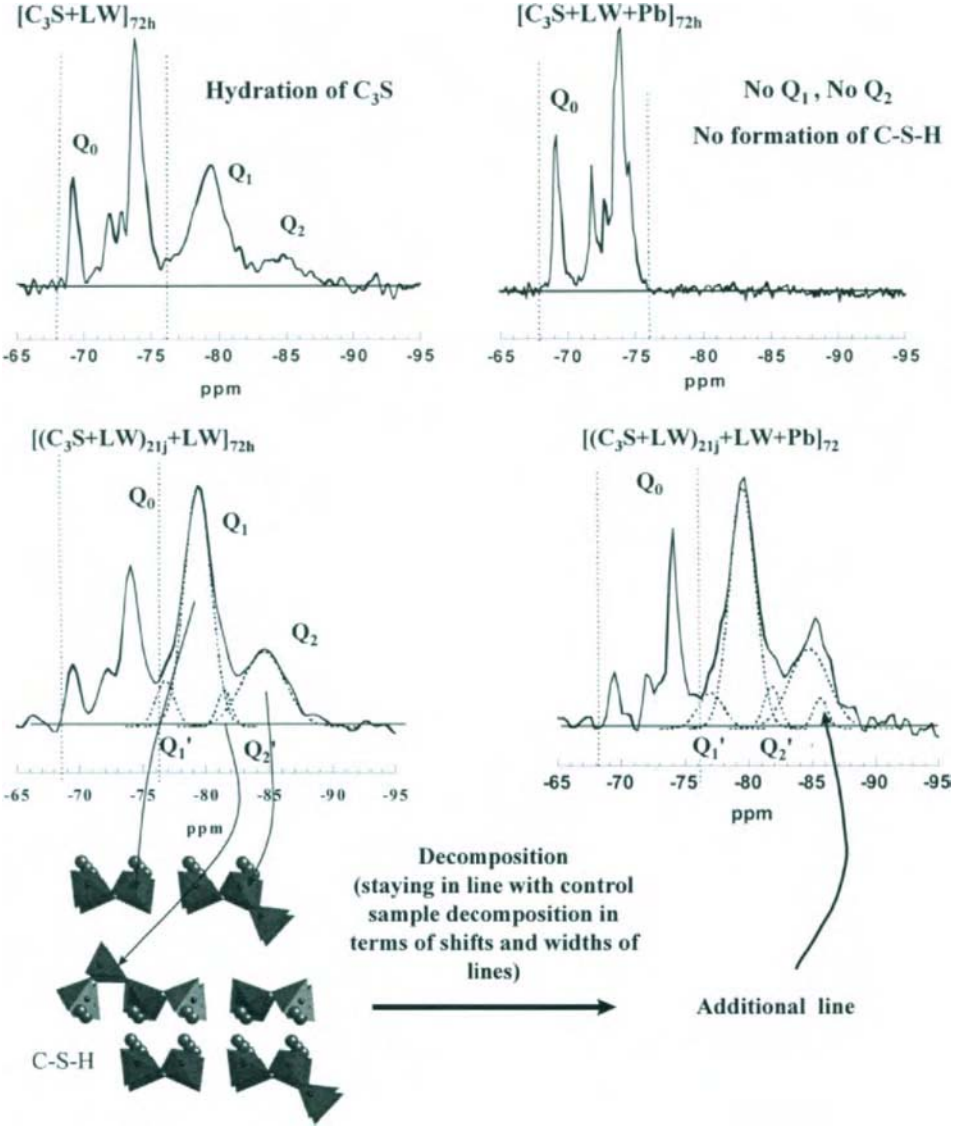


Table 2: Structural parameters for Cr-backscatterers contributions derived from EXAFS analysis.

Samples name	Atom	R(Å)	N	σ
$(C_3A+LW+Cr^{III})_{7d}$	O	2.01	5.8	0.058
	Ca	3.40	3.3	0.058
	Cr	3.51	2.7	0.067
$(C_3S+LW+Cr^{III})_{28d}$	O	2.01	5.8	0.067
	Si	3.47	6	0.060
	Ca	3.49	6	0.077
$[(C_3S+LW)_{21d}+LW+Cr^{III}]_{72h}$	O	2.01	5.8	0.071
	Si	3.32	4.6	0.104
	Ca	3.42	6.2	0.080

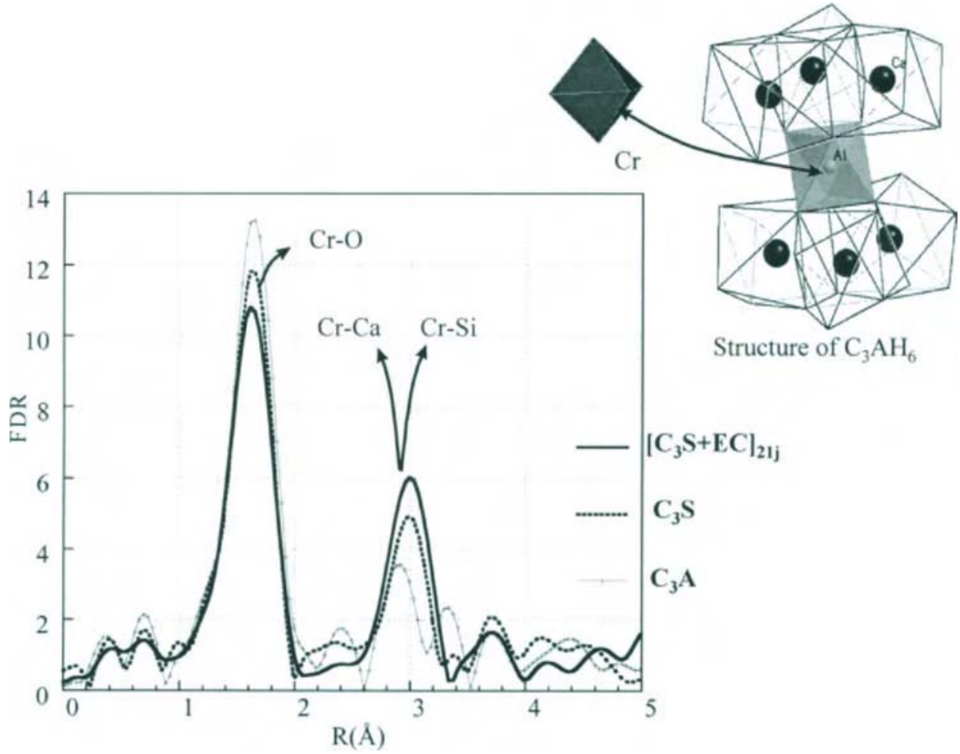
R : distance between Cr and backscatters, N : number of atoms, σ : Debye-Waller factor

Figure 5: ^{29}Si NMR spectra of $(C_3S+LW)_{72h}$, $(C_3S+LW+Pb)_{72h}$, $[(C_3S+LW)_{21d}+LW]_{72h}$ and $[(C_3S+LW)_{21d}+LW+Pb]_{72h}$, and decomposition of the hydrated part of $[(C_3S+LW)_{21d}+LW]_{72h}$ and $[(C_3S+LW)_{21d}+LW+Pb]_{72h}$.



retained by calcium silicate hydrated C-S-H and structural investigation methods reveal the existence of Si-O-Pb and Ca-O-Pb bonds.

Figure 6: Radial distribution functions of Cr K-edge EXAFS spectra of samples $[C_3A+LW+Cr^{III}]_{7d}$, $[C_3S+LW+Cr^{III}]_{28j}$ and $[(C_3S+LW)_{28d}+LW+Cr^{III}]_{72h}$.



Whereas lead shows a poor affinity to calcium aluminate phases (precipitation of PbO), it is strongly retained by hydrated phases coming from C_4AF hydration. As the main difference between hydrated phases coming from C_3A and C_4AF is the occurrence of hydrated ferrite phase, it seems reasonable to attribute this strong retention of lead to the hydrated "ferrite" phase.

4.2. Zinc

Out of sorption experiments, it appears clearly that zinc is strongly retained by calcium silicate hydrated This result has been also obtained by Ludwig et al. [12]. The use of structural investigation methods allows us to attribute this retention to the linkage of tetrahedral zinc to C-S-H tetrahedral silicates chains [2] [4].

The retention of zinc by calcium aluminate is essentially controlled by the precipitation of calcium hydroxyzincate. The strong retention of zinc by C_4AF is due to the presence of a hydrated "ferrite" phase. This assumption is confirmed by X-ray absorption spectroscopy results on which clear contribution of Fe-O-Zn bonds are displayed.

4.3. Chromium

Chromium oxidation state and its retention by hydrated cement phases are closely related. In the case of Cr^{III} and whatever the cement phases studied, an hydrogarnet phase of variable composition is formed (see EXAFS results). Cr^{VI} is weakly retained by calcium silicate, but in the case of calcium aluminate and aluminoferrite, a good retention is achieved. According to other results [4] and other authors [13] [14], ions exchange between CrO_4^{2-} and hydroxyl anions of the AFm phase are responsible for this retention.

5. CONCLUSION

Heavy metal retention sites could have been revealed thanks to the association of the experiments sorption and the use of two structural investigation methods. For each heavy metal considered in this study, there exists at least one case of strong retention. Several retention mechanisms could have been distinguished : (precipitation), surface sorption, ionic exchange, structural retention. Link strengths involved in heavy metals retention vary from one mechanism to another. The ability of heavy metals to be removed by leaching is controlled to a great extent by these strengths. Therefore, these interactions between cement hydrates and heavy metals should considered when conducting long term studies of cement leaching and its modelization.

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Thermal Treatment of Iron Oxide Stabilized APC Residues from Waste Incineration and the Effect on Heavy Metal Binding

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Iron oxide stabilized APC residues from MSWI were heat treated at 600°C and 900°C. The thermal treatments resulted in a change in product stability by forcing a transformation in the mineralogical structures of the products. The treatments, moreover, simulated somewhat the natural aging processes that would take place in a stabilized residue. Consequent changes in crystalline structure and heavy metal binding were examined.

1. INTRODUCTION

Air Pollution Control (APC) systems from Municipal Solid Waste Incineration (MSWI) produce great quantities of residue, rich in various heavy metals. A stabilization method, named the Ferrox process (Christensen et al., 2000), binds the contaminating heavy metals in an amorphous iron (hydr)oxide phase while salts are washed out simultaneously. The amorphous iron (hydr)oxides may over time transform into more crystalline and stable compounds with different physical and chemical properties and with different capacities for binding heavy metals. It is therefore important to evaluate the long term changes in the stabilized residues.

The iron oxide transformation, however, may be retarded significantly by contaminating ions, e.g. Si, present in the products (Cornell and Schwertmann, 1996) and it may, therefore, never take place under natural conditions. Ferrox treated residues were exposed to high temperatures, in order to force a transformation in the iron (hydr)oxide structure to take place and, thus, simulating long term changes or a potentionally additional technological step in the stabilization process. Changes in stability and metal binding capacity of the Ferrox stabilized residues were examined using various analytical techniques.

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2. MATERIALS AND METHODS

2.1. Stabilization

Fly ash (FA) from an electrostatic precipitator and APC residue from a semidry APC system (SD) were added to an $FeSO_4$ solution (L/S = 5 l/kg, 2.5 g Fe/100 g FA, and 5.0 g Fe/100 g SD). The solutions were stirred at their natural high pH for 24 hours, leading to the oxidation and precipitation of ferrous iron. The Ferrox treated products were then vacuum filtered and dried at 50°C. The content of selected metals in the two products is shown in Table 1.

2.2. Thermal treatment

Sub-samples of the two products were treated at either 600°C for three hours or at 900°C for 45 minutes in a Lindberg box furnace in a static uncontrolled atmosphere, the latter treatment simulating the typical residence time and temperature in a rotary kiln.

Mass balances were made, based on acid digestions of heated and unheated products in hot 7M HNO_3. The products used for this purpose were prepared somewhat differently from prescribed above, namely by precipitation at L/S 3 L/kg and a subsequent two stage washing using two times L/S 1 L/kg. The iron content of the two product were 1.5 g/100 g FA and 6.0 g /100 g SD.

2.3. Physical and mineralogical characterization

Differential and gravimetrical thermal analyses (DTA-TGA) were performed at a rate of 5°C/min between 25 and 1300°C on a Netzsch thermal analysis instrument model STA409. The analyses were conducted in air. X-Ray Diffraction (XRD) examinations were performed on a Phillips pw 1830 instrument, and physical examination of the surface was performed on a Scanning Electron Microscopy (SEM) instrument Jeol JSM 840 A. The surface area was determined using the BET method on a Quantasorb instrument, and the amorphous iron oxide fraction was quantified by extracting 2 hours in the dark in 0.2 M ammonium-oxalate. The iron oxide phase of the products were characterized using Mössbauer spectroscopy. Spectra were obtained in transmission geometry using a conventional constant acceleration spectrometer and a source of ^{57}Co in Rh at temperatures between 298 and 5 K and in external magnetic field up to 4 T.

Table 1

Content of selected metals in the Ferrox products after drying at 50°C (based on dry mass).

		Product[a]	
Element	Unit	SD	FA
Ca	g/kg	206	176
Fe	g/kg	53	32
Cd	mg/kg	182	246
Cr	mg/kg	151	262
Hg	mg/kg	27	3
Pb	mg/kg	6330	6575

[a] SD: Ferrox treated residue from a semi-dry APC system.
FA: Ferrox treated fly ash from an electrostatic precipitator.

2.4. Metal association and binding

The leaching behaviour of selected metals when exposed to an aquatic environment was examined in a pH static leaching test. Tests were performed over 24 hours at pH 6, 7, 8, 9, and 10 at a liquid to solid ratio (L/S) of 10 L/kg. pH was kept constant by automatic titration with HNO_3.

Kinetic extractions before and after thermal treatment revealed changes in metal binding. 30 ml 1 M HCl was added to sub-samples of approximately 0.1 g. After shaking for 15 minutes and up to 195 hours the extract was taken off. All samples were filtered through a 0.45 μm polypropylene filter and acidified prior to analysis.

2.5. Metal measurements

Metal analyses were conducted using AAS (graphite furnace and flame techniques), ICP-techniques (ICP-AES, ICP-SMS), and AFS (Hg measurements), depending on the metal and the concentration range.

3. RESULTS AND DISCUSSION

3.1 Thermal treatment

DTA analyses showed no significant transition temperature, where a change in the iron (hydr)oxide structure was taking place. A very broad exothermic peak was, however, observed around 800°C.

TGA showed a major mass loss in the temperature range 100-200°C, caused by the evaporation of chemically or physically bound water. Above approximately 1100°C a major mass loss was observed due to the evaporation of compounds and elements present in the treated products. Over the entire temperature range, between 200 and 1100°C, there was a continuous but less significant mass loss.

Acid digestions before and after heat treatment showed how particularly mercury had evaporated from the products. Only small fractions of Cd and Pb and possibly other elements like As, Co, Ni, and Zn had evaporated. When heating a fly ash based residual one may expect a larger fraction to be lost to the gas phase. The actual loss, is however, limited by the content of chloride, which was reduced significantly during the Ferrox treatment, thus resulting in a lower fraction of metals being evaporated as chloride salts.

The overall mass loss of the two products after heating, compared to the dry mass of the unheated products (dried at 110°C), were 7% for the 600°C treatment and 8-9% for the 900°C treatment.

3.2. Mineralogical characterization of the iron oxides

From oxalate extractions, XRD, and Mössbauer analysis it was clear that an initially amorphous iron oxide phase was transformed from a highly substituted ferrihydrite into a more crystalline structure upon heating, eventually forming hematite and/or maghemite after treatment at 900°C (results not shown). The latter structure was particularly found in the SD Ferrox product which initially had a minor content of activated carbon. The presence of carbon may, thus, be sufficient for the formation of locally reducing conditions in the sample while heating, and this, naturally, affects the iron oxide formation.

Thermal treatment at 600°C did not change the Mössbauer spectra significantly. The broad backgrounds formed from amorphous constituents in the samples were reduced in the

XRD diffractograms but Mössbauer analyses showed only minor changes in the spectra, thus indicating that a ferrihydrite structure still dominated in the product after three hours at 600°C.

As a natural consequence of the transformation process, the products both achieved a lower surface area and a more dense structure. Additionally, the oxalate extractable fraction of the iron was reduced, although a considerable fraction remained even after heating to 900°C (15% in the FA product and 34% in the SD product).

3.3. Heavy metal binding and release

Metal release measured by pH static leaching tests showed at pH 6-10 a significant pH dependency for all products but also differences between the heated and the unheated products were revealed. Based on the dry product mass, thermal treatment resulted in increased leachate concentrations for most metals (see selected metals in Table 2), and only the concentration of Cr showed a decrease after thermal treatment of the SD Ferrox product. This behaviour of Cr may, like the mineralogy of the heat treated SD product, be ascribed to the presence of organic carbon in the sample which may have acted as a reducing agent, thus forming highly insoluble Cr(III) compounds from Cr(VI) present in the sample prior to heating. The increased release of most other metals can be explained by various factors influencing the metal binding. Firstly, the decrease in surface area, as the iron oxides obtain a more crystalline structure, will result in a lower number of surface sites available for binding, hence making the metals more easily available for leaching. Secondly, the transformation in structure during thermal treatment may result in an outward solid state diffusion of cations initially trapped in the ferrihydrite. These cations may either be too large or too different in valency to fit in the newly formed crystalline iron oxide structure. This, again, results in a net increase in metals more easily released from the surface.

Table 2
Selected metals leached at pH 6-10 from the heat treated Ferrox products.
L/S = 10 L/kg. (μg leached metal / kg dry product mass).

		SD Ferrox			FA Ferrox		
Element	pH	50°C	600°C	900°C	50°C	600°C	900°C
Cd	6	15,200	52,700	10,700	14,900	59,600	34,000
	7	1,160	10,400	5,350	1,460	12,400	8,050
	8	131	1,370	967	137	1,780	1,130
	9	14	152	33	15	209	125
	10	1.7	34	6.4	2.4	31	12
Cr	6	6.1	321	3.6	2,040	1,080	955
	7	333	229	<2.0	6,630	10,900	10,200
	8	3,260	1,360	5.1	9,380	55,400	17,800
	9	398	6,060	32	6,470	56,600	24,400
	10	2,860	4,760	15	5,950	40,300	30,800
Pb	6	235	2,150	3,630	382	8,110	22,600
	7	18	230	500	52	715	196
	8	14.3	79	302	48	419	51
	9	<6.0	14	31	19	73	87
	10	<6.0	25	81	12	144	42

A few of the metals showed lower leachate concentrations after treatment at 900°C than after treatment at 600°C. This may be explained by a physical capture of these metals in structures sintered at 900°C, thus outbalancing the effect of the decreasing surface area. This fraction of cations is believed to be very well bound within the heat treated products.

Kinetic HCl extractions on the products revealed how iron oxide stability and distribution of Pb, Cd, and Cr in the products changed after a thermal treatment (Table 3). From this examination it was very clear how Pb came off readily, even before the dissolution of iron had started. This indicates an association of Pb to the surface only and does not show Pb as an integrated element in the iron structure or crystals. Cd and Cr did not show the same surface association, but a far slower release, partly dependent on the iron dissolution. Results for Cd and Cr indicated, on the contrary, that these metals were partly or fully integrated in the iron structure, depending on the Me/Fe ratio (results not shown). A completely congruent dissolution of Fe, Cd and Cr was, however, never obtained.

Table 3
Selected metals extracted in 1 M HCl (% extracted of total metal content) from the heat treated Ferrox products. L/S = 300 L/kg. Due to incomplete acid digestions some of the metals listed here reached extracted fractions higher than 100%. These have here been referred to as being 100%.

Element	Time	SD Ferrox			FA Ferrox		
	(hrs)	50°C	600°C	900°C	50°C	600°C	900°C
Cd	0.25	100	78	15	100	70	59
	1	100	85	19	100	75	62
	4	100	91	22	100	81	67
	24	100	93	26	100	85	67
	48	100	100	31	100	99	75
	195	100	100	38	100	100	97
Cr	0.25	57	51	0	65	51	16
	1	63	60	3	68	60	14
	4	63	66	7	68	66	19
	24	68	61	17	72	66	23
	48	73	71	29	73	76	28
	195	72	72	51	74	78	45
Pb	0.25	100	100	61	100	92	99
	1	100	100	68	100	95	94
	4	100	100	91	100	100	100
	24	100	100	100	100	100	100
	48	100	100	100	100	100	100
	195	100	100	100	100	100	100
Fe	0.25	88	60	7	84	42	17
	1	92	83	9	85	65	18
	4	92	84	12	87	73	22
	24	94	88	25	91	79	28
	48	100	95	39	89	90	37
	195	100	97	74	98	96	64

In the leaching tests Cd and Cr both showed a lower release from 900°C treated products than from 600°C treated products, whereas Pb clearly showed increases in leachate concentration as the treatment temperature was raised. These observations fit well with the kinetic extraction results, where Pb was found to be associated to the surface only, and, thus, never would be trapped in a sintered iron structure. Cd and Cr were, on the contrary, found to be more or less randomly distributed in the iron oxide crystals, and they were, therefore, much more likely captured in a fast forming crystalline structure.

4. CONCLUSIONS

By use of various analytical and environmental techniques we examined the effects of heating Ferrox stabilized APC residues. During these thermal treatments the stabilizing agent in the products, namely the iron oxides, transformed into crystalline and long-term stable hematite and/or maghemite structures. This change in structure naturally affected the physical properties and the metal binding properties of the products. The metal leaching properties generally changed within a factor of 5-10 after heating to 600°C or 900°C. Based on the initial dry mass of the products, leaching tests on heat treated products generally showed concentrations higher than prior to treatment.

From kinetic HCl extractions Pb was found to be associated to the surface only, whereas cadmium and chromium showed a slower release and, therefore, seemed to be integrated either partly or fully in the crystalline iron structure. Fractions of the two metals were, therefore, trusted to be very well bound in the products, which were furthermore believed to have reached a good stability towards changes in environmental conditions.

Thermal treatment of Ferrox stabilized APC residues does overall give a long term stable product but an initially high release of certain metals, e.g. Pb, cannot be avoided. All effects of heating must, therefore, be taken into account before a thermal step is added to the Ferrox stabilization process.

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On-site treatment and landfilling of MSWI air pollution control residues

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APC-residues from MSWI are difficult to landfill due to substantial leaching of trace metals. An on-site pre-treatment prior to landfilling of APC-residues is suggested. The treatment involves mixing of APC-residues with a ferrous sulphate solution and subsequent oxidation of the suspension. Bench-scale experiments were carried out with both a semidry APC-residue and a fly ash. After mixing and oxidation the suspension was transferred to model landfills to simulate on-site treatment and landfilling. The waste water from the process, which ran off through the drainage system, contained large concentrations of salts (Cl: 14-30 g/l, Na: 4-9 g/l, K: 5-11 g/l and Ca: 2-12 g/l) but low concentrations of Pb (14-100 μg/l) and Cd (<2-7 μg/l). The treated residues which were left in the model landfills were leached. The leachate contained low concentrations of trace metals (Pb: < 120 μg/l, Cd: < 1.7 μg/l and Cr < 485 μg/l). Colloids larger than 0.4 μm were not important as a transport medium for Pb, Cd, and Cr in this experiment. Substantial reductions were observed compared to a similar leaching of untreated APC-residues. Particularly, the initial release which was reduced by up to 4 orders of magnitude.

1. INTRODUCTION

Air pollution control (APC) residues from municipal solid waste incineration (MSWI) is produced in large amounts in all countries, where MSWI is an important part of the waste management system (In DK: approx. 70 000 ton APC-residues/year). The residues are considered hazardous waste in several countries and are difficult to dispose of due to the leaching of high concentrations of salts (Cl, Ca, K, Na, and SO_4) and trace metals, especially Pb, but also Cd, Zn, Cr, and Hg. In the future this problem will increase within the EC, due to the implementation of the new EC-directive on the landfill of waste adopted on 27. April 1999 (Offermann-Clas, 1999). This will imply reductions of biodegradable waste going to landfills in the EC and probably increase significantly the amounts of MSWI residues produced. Pre-treatment of the APC-residue before disposal may be needed. Methods to prevent leaching from APC-residues include separation processes, solidification, chemical stabilization, encapsulation, sintering, and vitrification.

A new treatment process called the Ferrox-process has proven to be able to reduce the leaching of Pb, Cd, and other trace metals substantially (Lundtorp et al., 1999). This process builds on the well-established geochemical knowledge that many iron oxides are stable and able to bind substantial amounts of trace metals (Cornell and Schwertmann, 1996). The process is carried out by mixing the APC-residue with a ferrous sulphate-solution and subsequently oxidizing the suspension before separation of the treated residue and the waste water.

By this treatment salts are washed out whereas the trace metals are retained in the solids, . thereby leading to less leaching of salts and metals from the treated APC-residue. The waste water separated from the solids has a high content of salts and a low content of trace metals. Ferrous sulphate is a by-product in titanium production and is therefore available at low cost.

An on-site treatment is suggested, where the pre-treatment is carried out in a mixing/aeration reactor at the landfill, using the drainage system of the landfills to separate the waste water from the solids by landfilling the suspension after oxidation, hereby simplifying the handling process. Due to the low content of trace metals in the waste water, this process could be a feasible solution depending on the site's possibilities to handle saline waste water and leachate. The suggested current treatment process has a number of advantages. E.g. it is based on retainment and does not yield a new waste fraction with trace metals, and the process is expected to be economically favourable due to simplicity, low energy consumption, and use of low cost chemicals.

2. MATERIALS AND METHODS

The experiments involved two different APC-residues from two large MSWI located in Denmark: a semidry gas cleaning residue containing fly ash and lime (SD) and a fly ash from an electrostatic precipitator (FA). A typical content of selected elements in these residues is given in table 1.

APC-residue (800 g) was mixed with a ferrous-sulphate solution (4 l) corresponding to 50g Fe^{2+}/kg semidry APC-residue and 25g Fe^{2+}/kg fly ash. The amount of iron added was limited by the alkalinity of the materials, in order to allow ferro-iron to precipitate as ferrohydroxides at high pH. After mixing the APC-residue with the ferrous-sulphate solution, the suspension was oxidized for 24 h with atm. air. The suspension was then transferred to a model landfill with a surface area of 0.2 m^2. The bottom of the landfill contained 4 different layers of sand and gravel with a drainage system in the bottom layer. Figure 1 shows the structure of the model landfill. The drainage layer was prewashed with deionized water.

In the model landfill the water runs off through the drainage system (called waste water) and the moist solids are left on top of the sand/gravel layers. On figure 2 an overview of the process is shown. This procedure was repeated 25 times over a period of 2 months, hence 25 layers of treated residue were built up on top of each other. The waste water was collected and sampled 25 times, once for each new layer. The material was not physically compacted.

After establishment of the two model landfills, one for each type of treated APC-residue, they rested for 2 months, before leaching with L/S 0.5 l/kg per week. The leaching was carried out by spraying the surface of the model landfills with deionized water with pH = 4 (adjusted with conc. HNO_3) equal to L/S 0.25 l/kg twice a week and using the drainage system for collecting leachate for sampling and analysis.

Table 1
Typical content of selected elements in semidry APC-residue (SD) and fly ash (FA).

	SD	FA
Cl (g/kg)	169	109
Ca (g/kg)	271	183
K (g/kg)	24	46
Na (g/kg)	26	38
Cd (g/kg)	0.15	0.21
Cr (g/kg)	0.11	0.23
Pb (g/kg)	3.98	6.37

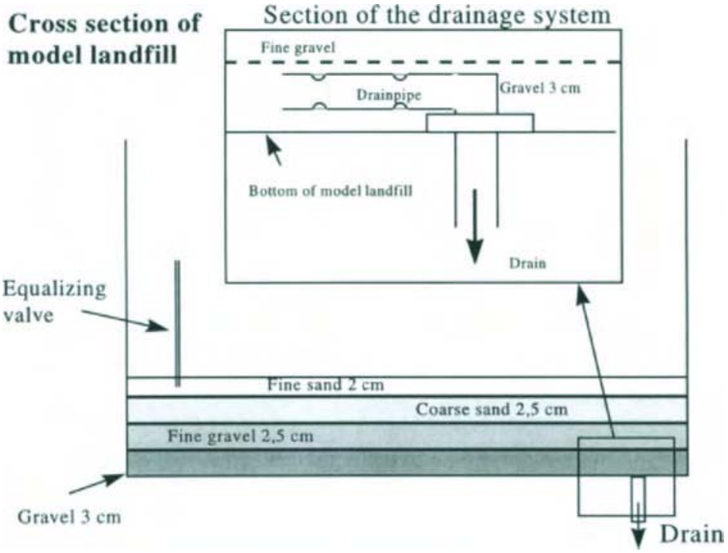

Figure 1. Structure of a model landfill.

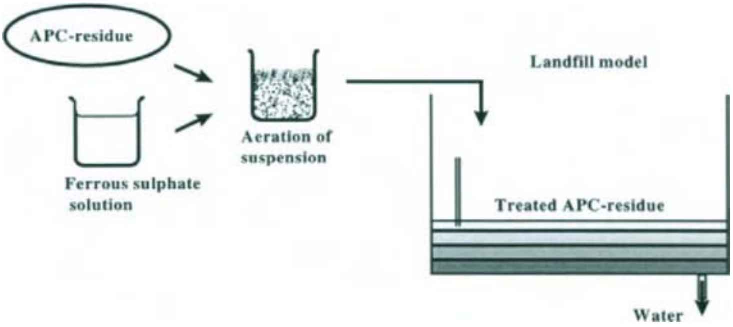

Figure 2. Overview of the on-site treatment and landfilling.

Parallel to the leaching of model landfills containing treated residues, model landfills containing untreated residues were established. This was done by humidifying the two untreated residues, corresponding to a moisture content of 20 % for SD and 25 % for FA. This equals the humidifying done prior to landfilling of the residues. The moist residue was then dispersed on a model landfill, identical to that shown on Figure 1, in portions equal to 800 g dry matter. This was done 25 times over a period of 3 months. After additional 2 months of rest, the model landfills with the untreated residues were leached in the same way as the model landfills with treated residues.

Samples were filtered through a 0.4 µm polypropylenefilter, and preserved with concentrated HNO_3 (pH between 1 and 2). Furthermore, selected samples of waste water and leachate from the model landfills containing treated residues were sampled as well without filtration. All samples were analyzed for pH, specific conductivity, Pb, Cd, and Cr. Pb, Cd, and Cr were analyzed by atomic absorption spectroscopy, using grafite furnace or flame techniques.

3. RESULTS AND DISCUSSION

3.1 Waste water

During active operation of a landfill using on-site treatment and landfilling the only wastestream leaving the landfill is the waste water removed through the drainage system. Therefore the content of this waste water is of special interest during the period of active operation. The concentrations of components in the waste water from model landfills containing treated residues are shown in Table 2. The waste water from the process contains relatively low concentrations of trace metals.

The content of trace metals in the waste water collected as landfill drainage did not differ from the content in the waste water prior to percolating through the model landfills (results are not shown). This was also the case for elements such as Cl, Na, K, and Ca. pH was 7.0-8.1 and 6.6-9.8 for the waste water from treatment of SD and FA, respectively.

Table 2
Concentrations of selected components in waste water from model landfills containing treated residues. SD is a semidry APC-residue and FA is a fly ash.

	SD	FA
Ph	7.0-8.1	6.6-9.8
Cond. (mS/cm)	64-75	61-69
Cl (g/l)	28-30	14-24
Ca (g/l)	11-12	2.1-2.3
K (g/l)	4.6-5.0	9.5-11
Na (g/l)	4.1-4.7	7.5-8.6
Cd (μg/l)	<2-3.7	<2-7.1
Cr (μg/l)	< 60	700-1100
Pb (μg/l)	14-86	19-100

The content of Pb and Cd in the waste water was low, but waste water from treatment of fly ash (FA) contained up to 1.1 mg Cr per l. Reducing the Cr content might be needed and ongoing research focuses on this issue.

Filtration at 0.4 μm did not significantly change the composition of the waste water compared to no filtration. Therefore, the trace metals were not considered to be associated with colloids larger than 0.4 μm in the waste water.

On Figure 3 it can be seen that pH and conductivity reaches a relatively stable level. Initial the conductivity is low due to dilution (the drainage layers had a initial content of water). Likewise initial pH is probably buffered by the drainage layers and therefore lower in the start.

The on-site treatment yields waste water with a high content of salts. This can, due to the low content of trace metals, potentially be discharged to a marine recipient, possibly after reducing pH by a simple aeration. The latter has been tried out and is without any difficulties (Lundtorp et al., 1999). In non-coastal areas an evaporation of the water is an alternative. The recovered salts could possibly be recycled for use as de-icing agents on roads.

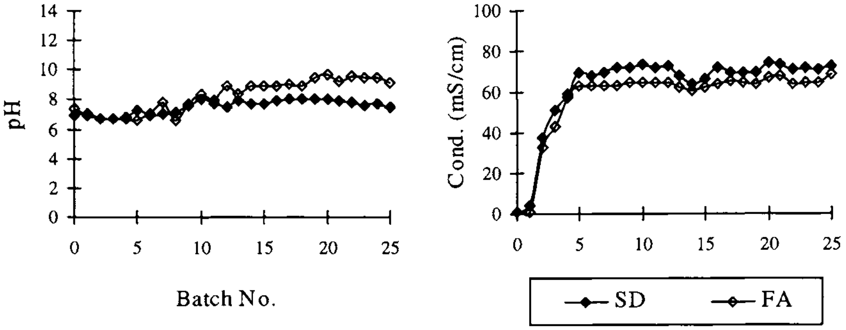

Figure 3. pH and specific conductivity in the waste water as a function of the number of batches of treated residues landfilled. SD is a semidry APC-residue and FA is a fly ash.

3.2 Leaching

After on-site treatment and landfilling of the residues the landfill is left in passive operation. This means that the landfilled residues is leached slowly by percolating rain.

Leaching of the model landfills showed that the treatment reduces pH in the leachate with 1 - 4 pH units (Figure 4). This is partly due to the $FeSO_4$-treatment and partly to the carbonization taking place when the treated APC-residue is spread on the landfill. It can be seen from Figure 4 that the conductivity is initially reduced in leachate from the treated residue. This is due to the removal of salts such as Cl, Na, K, and Ca during the treatment, as also suggested by the composition of the waste water (Table 2).

On Figure 5, the accumulated leaching of Pb, Cd, and Cr as a function of the liquid to solid ratio (L/S) is shown for model landfills with treated SD and FA and for model landfills with untreated SD and FA. From Figure 5 it can be seen that the treatment reduces the initial leaching by up to 4 orders of magnitude. The reduction could be partly due to the lowering of pH (van der Sloot et al., 1997), but previous work (Lundtorp et al., 1999) has shown substantial reductions in the leaching of Pb by pH-static testing. Therefore the reduction is not just a pH effect. The high leaching of Cd from the untreated residues with high pH suggests that Cd release from the untreated residues could be partly controlled by complexation with Cl^-.

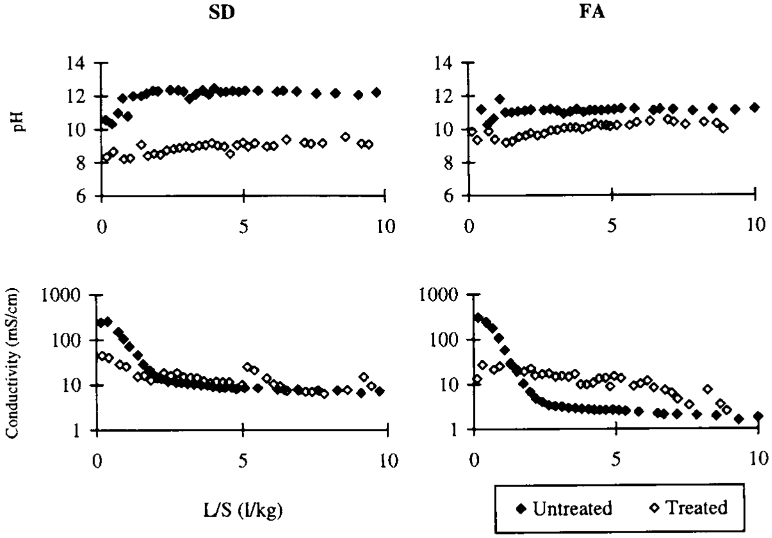

Figure 4. pH and conductivity in the leachate from model landfills with treated and untreated APC-residues as a function of the liquid to solid ratio (L/S). SD is a semidry APC-residue and FA is a fly ash.

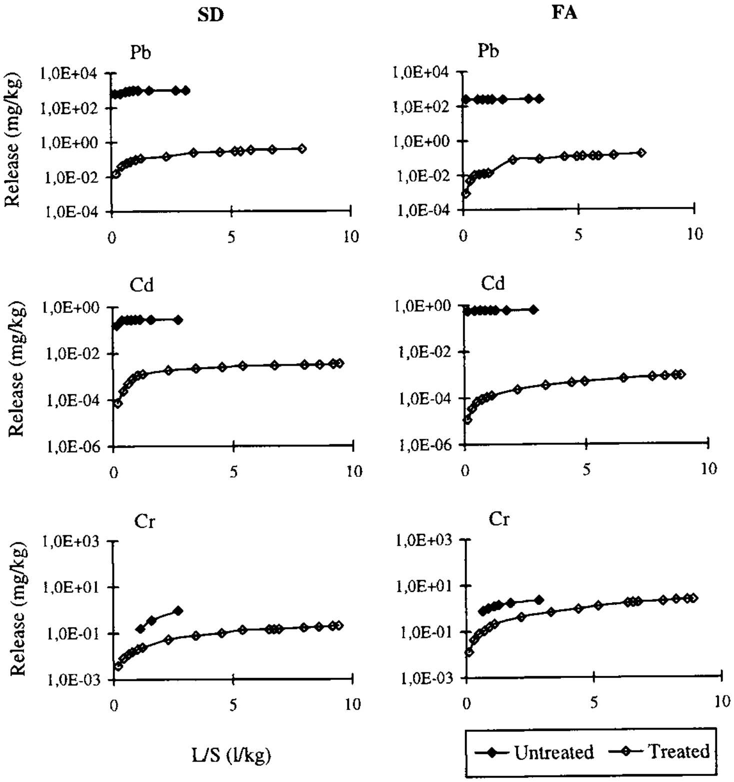

Figure 5. Leaching of Pb, Cd, and Cr from model landfills with treated and untreated APC-residues as a function of the liquid to solid ratio (L/S). SD is a semidry APC-residue and FA is a fly ash.

However the amount of Pb, Cd, and Cr bound to colloids larger than 0.4 μm is, in all cases, low. This suggests that the drainage system used generally is able to prevent migration of Pb, Cd, and Cr associated with larger colloids.

3.3 Physical properties

The total thickness of the 25 layers of treated residue was 17 cm for the treated semidry residue (SD) and 15 cm for the treated fly ash (FA). The dry matter content of these layers is 30-32 % for the treated semidry residue (SD) and 33-36% for the treated fly ash (FA). The treated semidry residue (SD) was soft with low carrying capacity (not quantified), but leaching hardened it, so it became firm. In contrast, the treated fly ash was firm even before leaching started. The geotechnical properties of the material will be evaluated later.

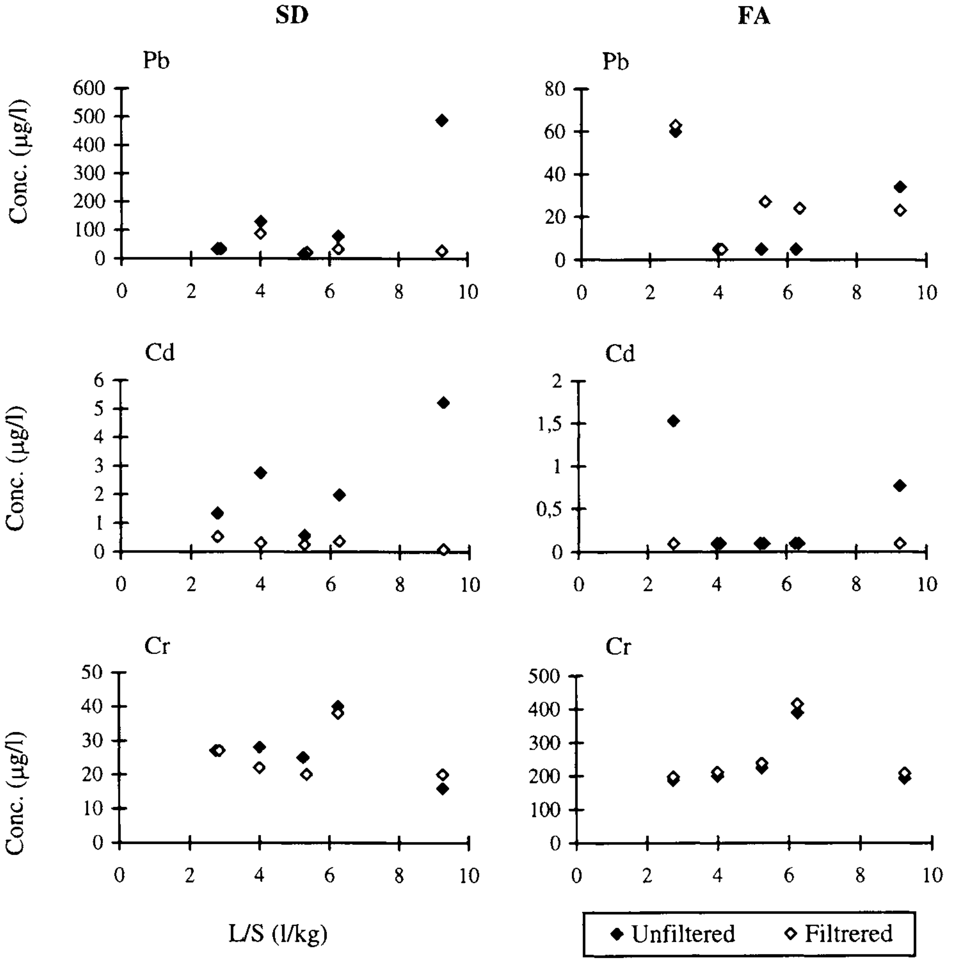

Figure 6. Comparison of selected samples from leaching of treated APC-residues, sampled with and without filtration. SD is a semidry APC-residue and FA is a fly ash. Filtration is done with 0.4 µm filters.

3.4 General discussion

The pretreatment of the APC-residues produces a waste water high in salt content, but low in trace metal content, and a solid material that has significantly improved properties with respect to landfilling. Pretreating the residues substantially reduces the release of Pb and Cd during passive operation of the landfill. Especially the high release with the first leachate is avoided by treating the residues. The first leachate generated during passive operation corresponding to L/S 2 l/kg may correspond to 130 years of full scale leaching (percolation: 200 mm/y, est. density 1.3 kg/l, height of landfill 10 m) and is therefore important both with respect to the surrounding environment and the costs of passive operation (leachate collection and treatment) of the landfill.

The total release during treatment (active operation) and leaching (passive operation) until L/S 2 is shown in table 3. From this it can be seen that the treatment overall reduces the release of Pb and Cd. Whereas Cr is reduced for the semidry residue and increased for the fly ash.

In table 4 the distribution of the total release during treatment and subsequent leaching until L/S 2 l/kg is shown. When using the treatment most of the release of Cd and Cr is done with the waste water compared to the amount released during leaching until L/S 2 l/kg. Pb is released more evenly.

It seems likely that a landfill drainage system consisting of gravel and sand is adequate to withhold the treated residue. However, the experiment showed that the hydraulic conductivity is low (water builds up on top of both model landfills). This aspect have to be addressed before on-site treatment and landfilling, because this could affect the landfill design. When landfilling a stabilized APC-residue, the long-term stability is an important issue. Further work will therefore focus on the long-term stability of the product by addressing the type and stability of the iron oxides formed, and the release controlling factors.

Table 3
The total release of Pb, Cd and Cr during active and passive operation until L/S 2 l/kg for untreated/treated residues and the relative reductions in release by treating the residues. SD is a semidry APC-residue and FA is a fly ash.

	SD			FA		
	Untreated mg/kg	Treated mg/kg	Reduction %	Untreated mg/kg	Treated mg/kg	Reduction %
Pb	990	0.28	99.97%	260	0.18	99.93%
Cd	0.29	0.0092	96.83%	0.61	0.011	98.20%
Cr	0.52	0.15	71.15%	1.9	2.9	-52.63%

Table 4
The distribution of the total release of Pb, Cd and Cr during active and passive operation until L/S 2 l/kg for treated residues. SD is a semidry APC-residue and FA is a fly ash.

	SD		FA	
	Active	Passive	Active	Passive
Pb	50%	50%	67%	33%
Cd	82%	18%	98%	2%
Cr	68%	32%	86%	14%

4. CONCLUSION

On-site treatment of APC-residues seems feasible with the Ferrox-process. The treatment reduces the leaching of Pb and Cd substantially, especially in the initial leachate, where reductions up to 4 orders of magnitude are observed. The total release of Pb and Cd which also account for the release during treatment (passive operation) is likewise reduced several orders of magnitude. A comparison of the release during treatment and the subsequent leaching show that most of the release is done during the treatment. The experiment showed that a simple sand/gravel drainage system is able to prevent migration with the waste water and leachate of Pb and Cd bound to colloids larger than 0.4 μm across. The waste water from the process contains low concentrations of Pb and Cd, and moderately low concentrations of Cr. As intended a large amount of salts is removed from the residue during the treatment, leading to a decrease in leaching of salts.

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Stabilization of waste incinerator APC-residues with $FeSO_4$

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This paper describes a new treatment process to reduce leaching of trace elements (Pb, Cd a.o.) and salts from waste incinerator air pollution control (APC) residues. The process involves mixing of the APC residues with a ferrous sulphate solution and subsequent oxidation of the suspension. The treated product has a significantly reduced content of salts and the heavy metals are bound by the iron oxides formed. The process has been tested on a semidry gas-cleaning residue and a fly ash. The treated products were characterized by leaching tests including pH-static tests. The generated wastewater contained relatively low concentrations of trace elements (e.g. Pb: 29-162 μg/l and Cd: 3.3-7.5 μg/l), but high concentrations of salts (e.g. Cl, Na, K, and Ca). The treatment process reduces the leaching of Pb from the residues by more than two orders of magnitude at fixed pH. Likewise, the Cd leaching was significantly reduced. Similar results were observed for Zn and Cu. The effect on elements that form oxyanions is more uncertain and in the current process there is no reduction in the release of Hg.

1. INTRODUCTION

Air pollution control (APC) residues from municipal solid waste incineration are produced in large quantities in all countries, where incineration is an important part of the waste management system (approx. 70 000 ton/year in Denmark). The residues are considered to be hazardous wastes in some countries (e.g. Denmark and the Netherlands). They are difficult to dispose of due to the leaching of high concentrations of salts especially Cl, Ca, K, Na, and SO_4 and trace metals, especially Pb but also Cd, Zn, Cr, and Hg. Pretreatment of the APC-residue before disposal may be needed. Methods to prevent leaching from APC-residues include separation processes, solidification, chemical stabilization, encapsulation, sintering, and vitrification.

In the present work a treatment process, called the Ferrox-process, is described involving mixing of the APC-residue with a ferrous sulphate-solution and subsequent oxidation of the suspension. This treatment process washes out salts and retains the trace metals in the solids, thereby leading to less leaching of salts and metals from the treated APC-residue. The treatment process builds on the well-established geochemical knowledge that many iron oxides are stable and able to bind substantial amounts of trace metals

(Cornell and Schwertmann, 1996). The wastewater separated from the solids has a high content of salts and a low content of trace metals.

Ferrous sulphate is a byproduct in titanium winning and is therefore available at low cost. The suggested current treatment process has a number of advantages. It is based on fixation of the metals in the residues and does not yield a new waste fraction with trace metals (for example from cleaning of a metal containing wastewater). In the future, the ferrox-process might be combined with solidification or other strategies. The treatment process is expected to be economical favourable due to simplicity, low energy consumption, and use of low cost chemicals.

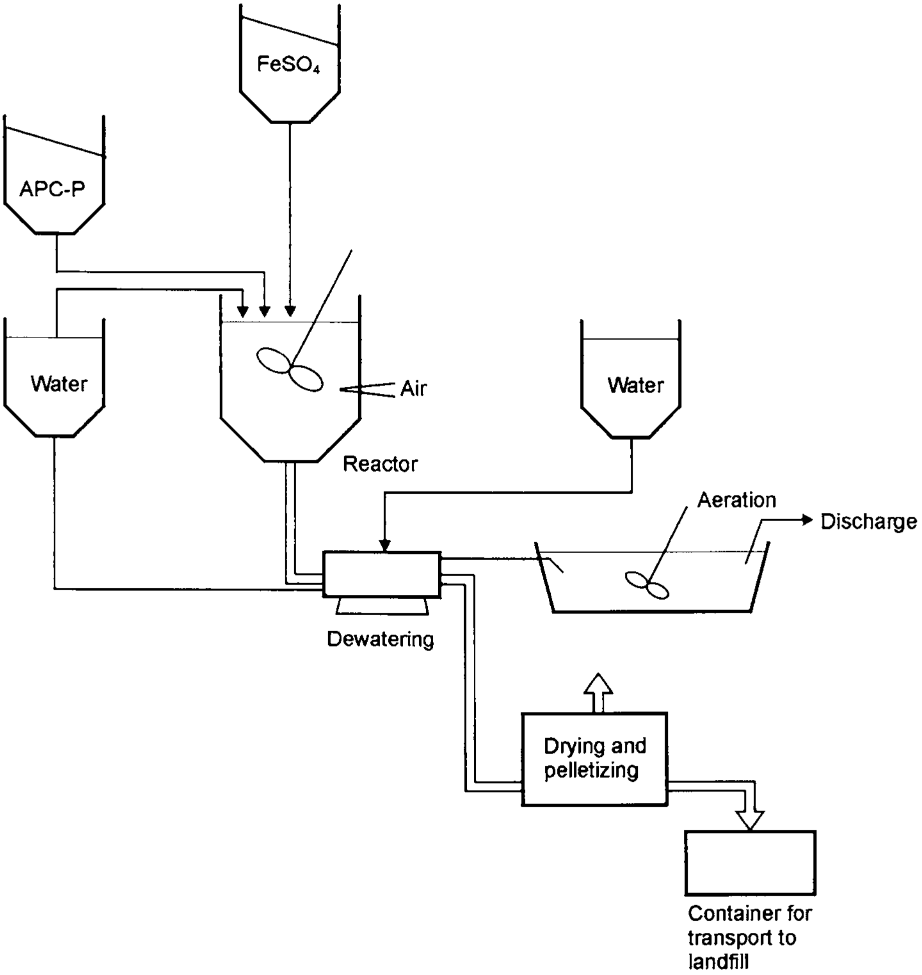

Figure 1. Schematic view of the treatment process.

2. MATERIALS AND METHODS

The experiments involved two different APC-residues from municipal solid waste incineration: a semidry gas cleaning residue containing fly ash and lime (AF) and a fly ash from an electrostatic precipitator (VF). APC residue (800 g) was mixed with a ferrous sulphate solution (4 l) corresponding to 50g Fe^{2+}/kg semidry APC or 25g Fe^{2+}/kg fly ash. Ferrous sulphate ($FeSO_4 \times 7H_2O$) of industrial quality with a natural content of ½-1 % sulphuric acid was used. The amount of iron added was partly limited by the easily available alkalinity of the materials, in order to allow ferro-iron to precipitate as ferrohydroxides at high pH. After mixing of the APC-residue with the ferrous sulphate solution the suspension was oxidized for 24 h with atmospheric air by intensive stirring. The suspension turned red after approx. 4 hours of stirring, which indicated oxidation of the ferrous iron to iron oxides. Current pilot-scale testing suggests that the aeration time in a designed plant will be less than one hour. The solids were separated from the wastewater by filtration. Afterwards the wet product was dried at room temperature resulting in approx. 90 % dry matter content. The treatment technology is sketched in Figure 1.

The treated residues were each characterized once by a CEN batch leaching procedure and pH-static tests. The CEN-test was carried out according to the guidelines given by the European Committee for Standardization, procedure C (1996) as a two-stage batch test (L/S 2 l/kg for 6 hours and 2-10 l/kg for additional 18 hours. Sample size: 75 g). pH-static testing was performed over a wide range of pH (pH 5-11) at L/S 10 l/kg for 24 hours, with computer controlled pH and addition of HNO_3. Likewise untreated residues were characterized. The samples, as well as the wastewater generated by the treatment, were analyzed for pH, specific conductivity, Cl^-, Ca, Na, K, Mg, Al, Fe, S, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn.

3. RESULTS AND DISCUSSION

3.1 Wastewater

The concentrations of components in the wastewater are shown in Table 1. The wastewater contains relatively low concentrations of trace metals, whereas large amounts of salts were transferred to the wastewater as intended. In Table 2 the dissolution of salts is shown as a percentage of the original content of the APC residues. It can be seen that the treatment removes the main part of the Na, K and Cl from the residues, but only a minor part of the Ca and S. For S the removal is 3% and 13% for AF and VF, respectively, if the added sulphate is corrected for. Part of the reason for this relatively insignificant removal of Ca and S is that Ca and S precipitate as gypsum and the removal of these elements is then controlled by the solubility of gypsum, whereas the more soluble salts such as Na, K, and Cl readily dissolve. The removal of trace metals was insignificant. The process removed e.g. 0.002 % - 0.01 % of the total content of Pb from the residues (results are not shown). The pH of the wastewater was relatively high and before discharging it was necessary to lower it. This was done by aeration. The two different wastewaters from treatment of semidry APC-residue and fly ash respectively were aerated, reducing the pH from 10.7 to 8 in a few hours. After the aeration was stopped the pH remained at 8 for the following 10 days.

Table 1
Concentrations of selected components in wastewater from treatment of a semidry APC-residue (AF) and a fly ash (VF).

	AF	VF
pH	10.7	10.7
Cond. (mS/cm)	73.6	62.3
Alk. (meq/l)	2.0	2.5
Cl (g/l)	27.0	17.5
Ca (g/l)	10.7	2.1
K (g/l)	4.1	8.7
Na (g/l)	4.0	6.8
Fe (mg/l)	0.15	< 0.1
S (mg/l)	370	1000
As (μg/l)	< 700	< 700
Ba (μg/l)	2110	750
Cd (μg/l)	3.3	7.5
Co (μg/l)	< 26	3.0
Cr (μg/l)	< 200	320
Cu (μg/l)	75	54
Hg (μg/l)	3.0	2.5
Mn (μg/l)	22	72
Mo (μg/l)	670	1700
Ni (μg/l)	< 300	39
Pb (μg/l)	162	29
Zn (μg/l)	148	37

Table 2
Dissolution of selected elements during treatment of a semidry APC-residue (AF) and a fly ash (VF) in percentage of initial content.

	AF	VF
Cl	90%[1)	95%[2)
Ca	21%	7%
K	98%	93%
Na	87%	83%
S[3)	5%	20%

[1) Based on a typical content of 150 g Cl/kg residue from this specific MSWI plant.
[2) Based on a typical content of 92 g Cl/kg residue from this specific MSWI plant.
[3) Based on the residues content of S and without considering the added sulphate.

In order to evaluate if the wastewater was supersaturated with respect to any minerals, with a potential for later precipitation, for example, in a discharge area, the composition of the wastewater was modeled by a speciation program MINTEQA2 (Allison et al., 1991). The modeling was based on the values in Table 1 at 25 °C. Fe was not included in the modeling. In Table 3 the species that are supersaturated are listed with the obtained saturation indices. Several of the minor minerals showed supersaturation. Anhydrite and gypsum were according to the saturation indices, the only major species that could have precipitated in substantial amounts (sulphate was added during the process). However, no precipitates were observed during the aeration of the wastewater. This might be due to fact that the MINTEQA2 model cannot handle such high salinity as in the case of the actual wastewater, and thus overestimates the ion activities. Therefore the modeling results only serve as an indication.

The wastewater had a composition similar to sea water and a possible way of handling is to discharge it to a marine recipient. However, this is not an option in non-coastal areas, where evaporation could be a possibility. The salts from the evaporation might be recycled for use as de-icer on roads or as industrial chemicals.

A mass balance for the treatment process is shown in Table 4. The wastewater removes 18 -23 % of the original mass of the residue, but the build up of iron oxides and the precipitation of gypsum in the product result in overall mass loss of 9-11%.

Table 3
Saturation indices of species (log(IAP/K)), which are supersaturated according to modelling by MINTEQA2.

	AF	VF
Anhydrite ($CaSO_4$)	0.384	0.265
Barite ($BaSO_4$)	1.498	1.687
Diaspore (AlOOH)	0.074	1.035
Gypsum ($CaSO_4 \times 2\ H_2O$)	0.574	0.459
Tenorite (CuO)	0.270	0.077
Zincoxide (ZnO)	0.147	us
$Pb(OH)_2$	2.655	1.848
$Pb_2(OH)_3Cl$	1.952	0.093
$Ni(OH)_2$	us	1.837
Bunsenite (NiO)	us	0.195

us: Undersaturated

Table 4
Mass balance for the treatment of 1 kg residue. All values are in g/kg residue

	AF	VF
Added Fe^{2+}	50	25
Added SO_4^{2-}	86	43
Added O_2 [1)]	7	4
Dissolved	-231	-181
Weight loss/increase	-88	-109

[1)] O_2 bound in the formed iron oxides. 0.25 mol O_2 per mol Fe^{2+}.

3.2 Leaching

Table 5 and Figures 2 and 3 show the results of the CEN-test and the pH-static leaching test for selected components. The results for Cd show a decreasing accumulated release (Figure 2). This is caused by uncertainty in measuring at low concentrations in solutions with high salinity together with problems in separation of solid and liquid at L/S 2 l/kg. The latter means that a major part of the ions measured in the second stage of the batch test is leached in the first stage, thereby making it difficult to register a minor increase.

The results show that the leaching of Cl, K and Na is reduced. A large part of these components in the treated residue originates from residual wastewater, since there is a residual water content in the solids after separation of solids from wastewater corresponding to approximately L/S 1 l/kg. The treated residue is dried before the leaching experiments. By this drying procedure the residual wastewater evaporates thereby leading to precipitation of salts, which afterwards are readily available for leaching. Due to this effect, the leaching of easily soluble salts is likely to be strongly dependent on the separation of solid and liquid.

The leaching of Pb was generally reduced by two orders of magnitude at fixed pH and up to four orders of magnitude at the CEN-test. The very large reduction in the leaching of Pb in the CEN-test is partly due to the pH-decrease induced by the treatment process. pH is higher in the untreated residues compared to the treated residues (Table 5), which affects the leaching of Pb due to the amphoteric behavior of Pb. Likewise, the leaching of Cd was significantly reduced according to the pH-static-test. Generally by about two orders of magnitude. At the natural pH for untreated residue (pH>11), the Cd released from the untreated material was expected to be limited by the solubility of cadmium hydroxide, and thus the effect of the treatment is less significant at this pH.

Table 5
Concentration in first stage of a CEN-test (L/S 2 l/kg) on a treated and an untreated semidry APC-residue (AF) and a fly ash (VF).

	AF		VF	
	Untreated	Treated	Untreated	Treated
pH	11.4	9.7	11.6	8.9
Cond. mS/cm	150	51	130	23
Cl (mg/l)	76500	16000	57000	7310
Ca (mg/l)	29400	8520	3230	1330
K (mg/l)	9300	2000	21200	2230
Na (mg/l)	9400	2080	16500	2010
S (mg/l)	270	350	1070	674
Ba (μg/l)	4300	2690	1740	406
Cd (μg/l)	18	3.8	26	5.4
Cr (μg/l)	50	400	<25	1410
Hg (μg/l)	130	50	0.36	12
Cu (μg/l)	<330	<20	430	11
Pb (μg/l)	388000	36	1470	16
Zn (μg/l)	17800	71	2850	31

The leaching of Zn and Cu is comparable with that of Pb and Cd, respectively. There is a significant reduction in the leaching of these two elements. Currently, the process does not reduce the leaching of Hg. The release of Cr is increased due to the lower pH in the treated residue. These subjects are to be addressed in future research.

Overall, the treatment process shows positive results. However, it must be remembered that the test methods used are short-term tests, and since the treatment process is based on the formation of an iron oxide phase, the stability and nature of the formed iron oxides must be addressed in future research.

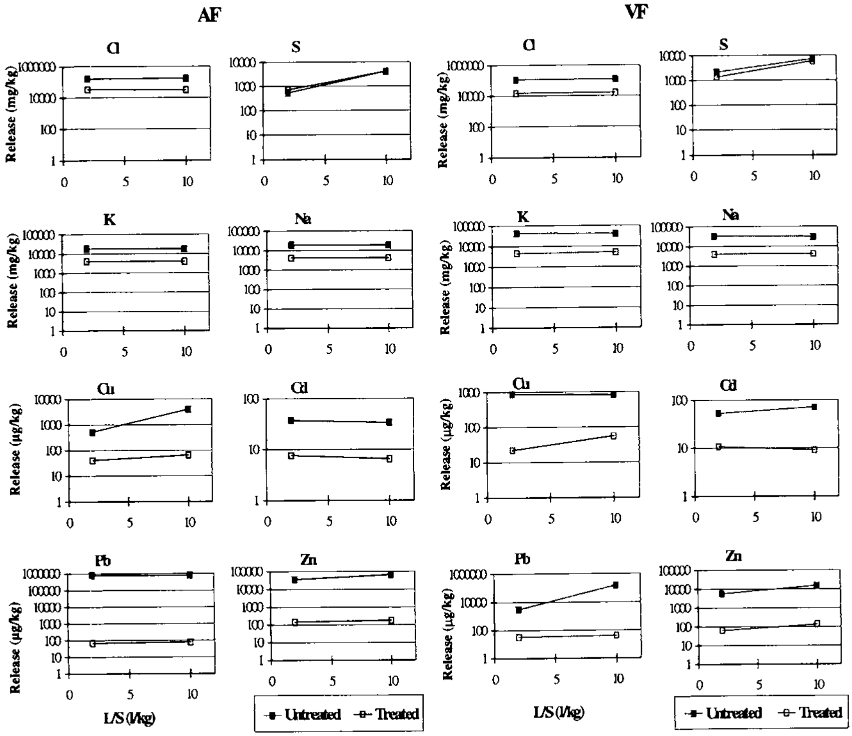

Figure 2. Results of CEN-test on a treated and an untreated semidry APC-residue (AF) and a fly ash (VF) as release vs. L/S-ratio for selected elements.

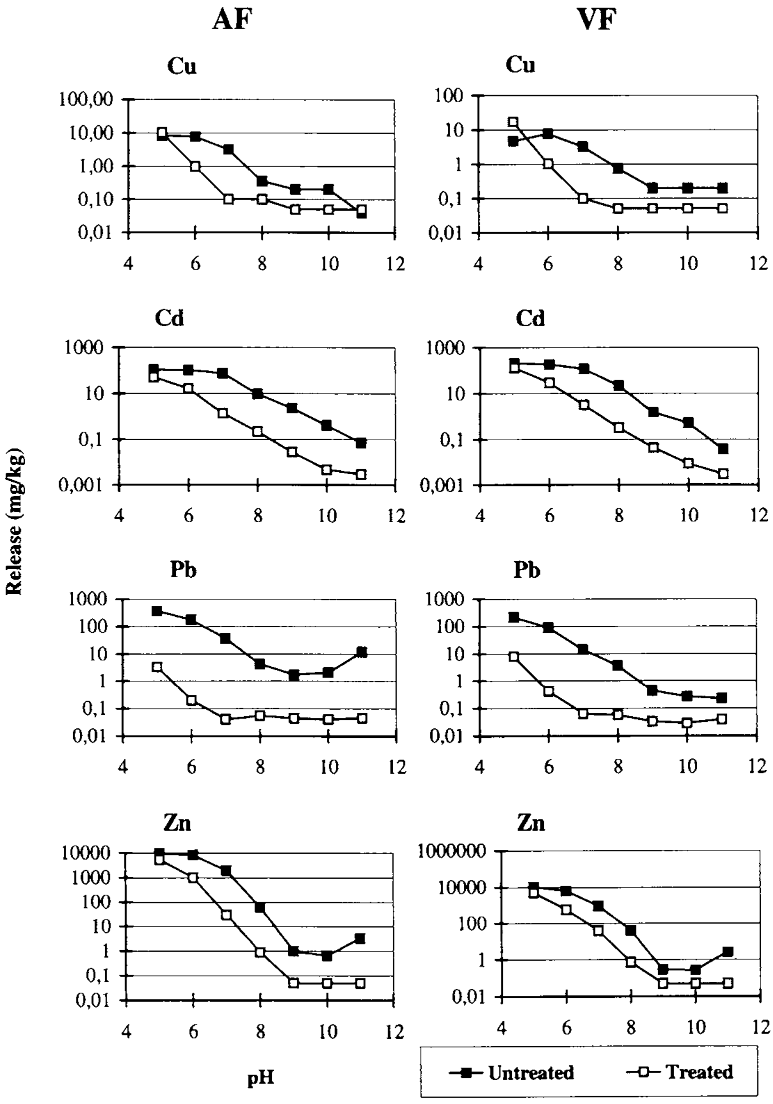

Figure 3. Results of pH-static leaching tests on a treated and an untreated semidry APC-residue (AF) and a fly ash (VF) as release vs. pH for selected metals.

4. CONCLUSION

Treatment of semidry-APC and fly ash with ferrous sulphate significantly improves the leaching properties of the residues with respect to Pb, Cd, Zn, Cu, a.o. The release of Pb is reduced by up to four orders of magnitude at the natural pH of the two residues. At fixed pH the release of Pb is generally reduced by two orders of magnitude. During the treatment only insignificant amounts of these trace elements were removed from the residues and the wastewater from the process does not contain unacceptably large amounts of trace metals requiring treatment of the wastewater. With respect to the salts large amounts of Cl, Na, and K were removed from the residue during the process e.g. more than 90 % K and 80 % Na.

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Environmental Management in Tanneries – Waste Minimisation Opportunities

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This article is based on a survey, carried out in Franca, São Paulo State, Brazil, of the opportunities for waste minimisation in thirteen tanneries in that city, and the potential benefits for environmental management. Waste minimisation opportunities mean the feasibility of implementing practices or measures of waste reduction, pollution prevention and cleaner production, in relation to this industrial activity. This opportunity was defined in terms of waste minimisation indicators found in a bibliographical survey and in data obtained from field research done in those tanneries. Using this information, an "opportunity matrix" was created in order to identify and evaluate alternatives and possibilities for waste minimisation. Potential benefits for industry and the environment are also evaluated, on the basis of this matrix. A discussion about the development and application of the matrix is also presented.

1. INTRODUCTION

Industry is now facing environmental issues that go beyond the traditional concern with restricting liquid, solid and gaseous emissions, according to legal standards. Problems such as waste of resources, raw material and energy, dangerous waste disposal, workers' safety and health, waste minimisation, pollution prevention, cleaner production and environmental management, are generally major concerns nowadays. Moreover, corrective actions, or end-of-pipe practices, involve higher costs and have been demonstrated to be less effective.

As environmental issues become more and more complex, strategies for waste control and management also become more systematic and integrated. The importance of incorporating practices for pollution prevention and waste minimisation in the productive cycle is globally recognised. The main aim is to make products with better quality, while reducing the input of resources (raw materials, energy, etc.) and costs and generating fewer and lower impacts on the environment.

The tannery industry is one of the Brazilian industrial sectors where more efforts have been made to develop and implement pollution prevention and waste minimisation practices. In Brazil, there are nowadays about 700 tanneries, employing direct and indirectly about 48,000 workers, with an annual revenue of US$ 1.5 billion (1).

Tanneries, like many other industrial activities, have impacts on the environment, such as: harmful effects on surface water and aquatic life, soil and groundwater contamination, deterioration of air quality, and risk to human health, among others (2, 3). These environmental impacts are mainly related to wastes that are generated in the tanning process.

Such wastes can be liquid effluents from spent floats, solid wastes (organic, from animal source, and inorganic, composed of residuals of chemical inputs) and atmospheric emissions from chemical reactions, treatment of liquid wastes and from the activity of boilers. The pollution potential of those wastes varies, according to their quantity and degree of toxicity.

The field survey for this study was conducted in the town of Franca, located in São Paulo State, Brazil, which has the second largest leather-shoe industrial complex in the country. The town has an area of about 603 square kilometres and a population of 267,235 inhabitants (4). The monthly average production of leather is 650,000 square meters, with over 2,500 persons being employed directly. All the leather production is concentrated in sixteen tanneries, thirteen of which are located in the tannery industrial district of the town. The other three are dispersed around the town.

Regarding environmental issues, Franca has been facing problems about the disposal of tannery wastes, including those containing chromium. The monthly average generation of tannery solid waste in 1998 was 300 tons, this being disposed in the municipal landfill. The volume of liquid wastes is also high, resulting in costs up to US$ 0.50 per square meter of produced leather. Atmospheric emissions are not quantified.

To evaluate the potential of minimisation of industrial tannery wastes in Franca, a field survey took place on the thirteen tanneries located in the industrial district. The data and information obtained made possible the construction of an "Opportunity Minimisation Matrix". This matrix was used as a tool for analysis and evaluation of which tanneries are more suitable for the implementation of waste minimisation measures and which practices are more feasible.

Therefore, the aim of this article is to present criteria used in the analysis of the potential minimisation of tannery wastes, based on the concepts of cleaner production, pollution prevention, and the reduction, reuse and recycling of wastes.

2. METHODOLOGY

The present study was developed using, among other methods, two current methods of Environmental Impact Assessment (EIA): Checklist and Impact Matrix. These two methods were adapted in order to identify and analyse the opportunity for implementing of waste minimisation practices in tanneries. All the methods used are presented next:

a) Bibliographical survey of tannery processes, environmental aspects, practices and international experience in waste minimisation. This survey was done in research centres, sectoral institutions, environmental organisations and Internet.

b) Questionnaire with the aim of producing a broad profile of the tanneries, including the productive processes and environmental aspects, such as pollution and waste minimisation data (5). This questionnaire was directed to managers and process technicians.

c) Checklist containing the minimisation practices that arose in the survey (item a) and identifying environmental benefits of such practices.

d) Matrix of waste minimisation opportunities and environmental benefits, based on the LEOPOLD Matrix (6). The matrix was used to identify both the opportunity of implementation of waste minimisation practices and also their benefits. The matrix also assesses which tanneries are more suitable for the development of such practices, using a scale of valuation.

3. PROCEDURES

From the bibliographical survey and existing experience, possible actions for waste minimisation were identified, as well as their benefits. Next, the questionnaire was elaborated, covering a range of information, as follows:

- General data - address, number of employees, industrial activity, revenue, etc.;
- Inputs - type, quantity and usage of energy, water and raw material;
- Type of products and industrial production;
- Description of industrial processes and manufacturing operations;
- Current practices for cleaner production, pollution prevention and waste minimisation;
- Solid waste, wastewater and atmospheric emissions;
- Waste treatment and emission control;
- Information on environmental aspects: legal requirements, environmental impacts of industrial activities, expenditure related to environmental protection, etc.

Then, visits to the tanneries of Franca were made, to become acquainted with the industrial plants and processes, to apply the questionnaire to the managers and process technicians, and to gather data. A typical flow-chart of the tannery process could thus be drawn, with the industrial operations and their respective wastes (see Figure 1).

From the bibliographical survey, experience and information collected, and questionnaire answers, a checklist was elaborated, containing 47 possible waste minimisation practices in tanneries. This checklist is presented next, being the practices identified within each industrial process stage.

Checklist - Waste Minimisation Practices

Beamhouse Stage:

- Short-term preservation of hides, by antiseptic treatment (7);
- Freeze preservation of hides (7);
- Preservation of hides by electron-beam sterilisation (8);
- Preservation of hides with sodium chlorite (9);
- Recovery and valorisation of residual sodium chloride (7, 10, 11);
- Classification of hides according to the final product (leather) (12);
- Adoption of pre-soaking and pre-fleshing operations (12);
- Direct recycling of liming floats (7, 10, 13);
- Recovery and valorisation of hair (7, 10, 11, 14);
- Replacement of sodium sulphide by enzymatic and amine treatment (7, 10, 15, 16);
- Sulphide oxidation during the unhairing and liming operations (16, 17);
- Flesh valorisation (7, 18, 19);

Tanning Stage:

- Carbon dioxide deliming (7, 10, 12);
- Sulphide oxidation during the deliming operation (16);
- Deliming without ammonia products (7, 10);
- Recycling of pickling floats (7, 20);
- Use of non-tumefying acids together with formic and sulphuric acids in the pickling (15, 21);
- Use of oxidants in the pickling (10, 15, 16);
- Splitting operation before tanning (7, 10, 21);
- Shaving and trimming operations before tanning (7, 12, 21);

- High exhaustion tanning (10, 20, 22, 23);
- Direct recycling of chrome tanning floats (7, 10, 20, 23);
- Recovery and reuse of residual chrome, through precipitation (7, 20, 22, 23);
- Replacement of chrome, where possible, by other tanning agents (7, 23);

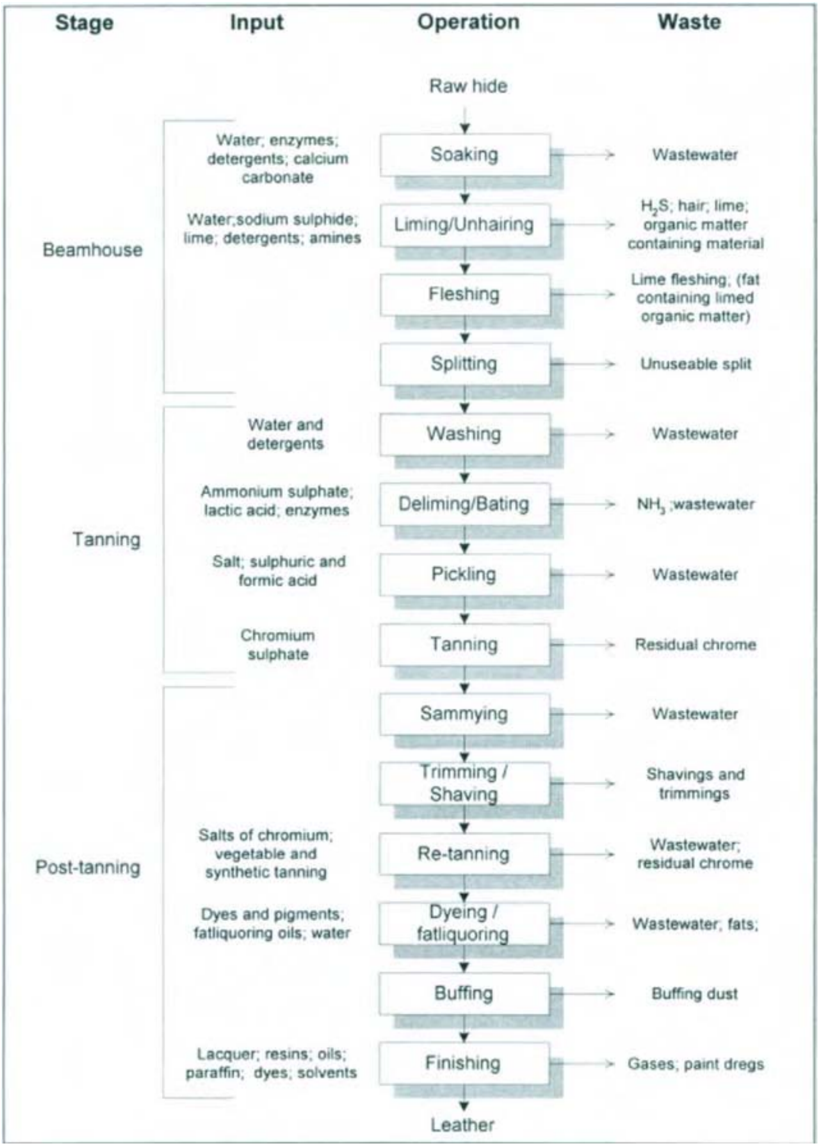

Figure 1. Tannery Process Operations and Respective Wastes.

Post-tanning (finishing) Stage:

- Valorisation of shavings (18, 19);
- Thermo-chemical destruction of shavings to recover chrome (24, 25);
- Use of acrylic polymers to fix the re-tanning chrome during the neutralization operation (10);
- Accomplishment of a single treatment by mixing re-tanning agents and fatliquoring products (12, 26);
- High exhaustion re-tanning (10);
- Recovery and reuse of residual chrome from the re-tanning operation, by precipitation (10);
- Replacement of chrome, where possible, by other re-tanning agents (26);
- High exhaustion dyeing (10);
- Continuous immersion dyeing (26);
- Infra-red drying, in a tunnel (27);
- Valorisation of buffing dust (18, 19, 28);
- Replacement of lacquer in a solvent base by urethane polymers in an aqueous emulsion (15);
- Using roller or cylinder for finishing coat, instead of spray application (7, 15, 26);
- Use of finishing products in aqueous base (7, 10, 26, 28);

Complete Process:

- Recovery and valorisation of residual sodium sulphide (2, 7);
- Automation of hide processing (12);
- Planning of water usage (2, 12);
- Planning of chemical products usage (12);
- Recovery of gases and particulates with capture equipment (7);
- Reduction of the stocking time of solid wastes (12);
- Valorisation of chemical product packing, if feasible (12);
- General cleaning and maintenance of machinery, equipment and work environment (2, 12).

In possession of the checklist and the preview survey on the tanneries, the opportunity matrix was built. This matrix is composed of a vertical list containing forty-seven possible waste minimisation practices previously defined in the checklist. These practices are classified according to the stage of the industrial process. The matrix is also composed of a horizontal list of the thirteen tanneries in the study.

The correlation between each tannery and each practice is made in the related matrix cell, through two attributed values or weights. The value A, in the bottom left-hand corner of the cell, represents the implementation opportunity of the practice. The value B, in the top right-hand corner, represents the benefit from this practice (see Figure 2).

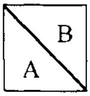

Figure 2. Scheme of a Matrix Cell.

Both values may vary from 1 to 3, according the degree of correlation between practices and tanneries, as follows.

Opportunity of minimisation practice implementation (A value)

- ☐ High opportunity: 3
- ☐ Medium opportunity: 2
- ☐ Low opportunity: 1

In some cases the value A can be considered as follows:

- ☐ Yet implemented: 3*
- ☐ Not applicable: na

The degree of opportunity of implementation of a practice is defined in terms of: physical structure and industrial lay-out, process operations, types of raw materials and products, waste characteristics, existing equipment, available cleaner technologies, cost of implementation of the practice, culture of the industry regarding environmental issues, intentions of the board of directors of the company to implement minimisation practices and so on.

Benefits of practices (B value)

- ☐ High benefit: 3
- ☐ Medium benefit: 2
- ☐ Low benefit: 1
- ☐ Undetermined benefit: ub

The degree of benefit is defined by taking into account direct financial gains (e.g. reduction of inputs or raw materials), indirect financial gains (e.g. better public image), potential for waste minimisation, environmental gains, decrease or end of non-compliance with legal requirements, etc.

To establish a relation between a minimisation opportunity and its benefit, the sums of the products of A and B values are indicated in the last column and last row of the matrix. This procedure results in a total valuation of opportunities plus benefits, indicating the synergetic effect between these variables. The total value, measured on a scale of 1.0 to 9.0, is useful to show the degree of opportunity associated to the importance of its respective benefit. For example, when there is a high opportunity and a high benefit, the sum is 9.0, resulting in a maximum synergetic effect. The total valuation is given by the following expressions:

$$\sum_{1}^{n} \frac{A \times B}{n} \qquad (1)$$

$$\sum_{1}^{m} \frac{A \times B}{m} \qquad (2)$$

Expression (1) refers to the last column of the matrix, n being the number of practices identified (forty-seven for this work). Expression (2) refers to the last row and m is the number of tanneries studied (thirteen in this case).

Finally, another visit to the tanneries was made, to check data, obtain more information and define opportunities and benefits with the aim of completing the matrix.

4. RESULTS AND COMMENTS

The first or major result is the Matrix of Waste Minimisation Opportunity shown in Figure 3, for the thirteen tanneries studied in Franca (tanneries A to M).

According to the matrix, the most important minimisation practices are six: replacement of sodium sulphide by enzymatic and amine treatment, high exhaustion tanning, high exhaustion re-tanning, chrome replacement by other re-tanning agents, high exhaustion dyeing, and use of water-based finishing products. These practices correspond to total valuations of 9.0 in the last column.

Another result is related to the priority tanneries, in other words, the tanneries which have more opportunity for the implementation of waste minimisation practices, taking into account environmental benefits. In the present work, these tanneries correspond to which ones with total valuations of more than 6.0, in the last row (tanneries A, F, H and L)

5. CONCLUSIONS

The methodology applied to the present work may be used for any type of industrial activity, not only for tanneries. The methods of Checklist and Impact Matrix, currently used in Environmental Impact Evaluation, can be satisfactorily applied to identify and evaluate waste minimisation opportunities. However, more research on the matter is needed.

The matrix affords an overview of the tanneries of Franca, with respect to environmental management and waste minimisation practices. The matrix just shows a general tendency, indicating opportunities, priority practices and priority industries for such practices. It can be used as an interesting and useful environmental management tool, as an auxiliary to decision making. On the other hand, the results have to be considered carefully, not as accurate information, but a trend indicator, as aforementioned. It is recommended that specific and detailed studies be done, for each case.

Acknowledgements

The authors are grateful to CNPq – Conselho Nacional de Pesquisa e Desenvolvimento Tecnológico, from Brazil, for the financial support to the research that resulted this article.

Stage	Operation	Waste	Minimisation practice	Result	Minimisation Opportunity													Total Value
					Tannery													$\sum_{1}^{n} \frac{A \times R}{n}$
					A	B	C	D	E	F	G	H	I	J	K	L	M	
Beamhouse	Raw hide and skin preservation	Residual NaCl	Short-term preservation of hides by antiseptic treatment	NaCl reduction in wastewater and environment	3* \ 2	3 \ 2	3* \ 2	1 \ 2	na	na	na	na	na	2 \ 2	na	na	na	4.8
	Raw hide and skin preservation	Residual NaCl	Freeze preservation of hides	NaCl reduction in wastewater and environment	2 \ 2	1 \ 2	1 \ 2	1 \ 2	na	na	na	na	na	2 \ 2	na	na	na	2.8
	Raw hide and skin preservation	Residual NaCl	Preservation of hides by electron-beam sterilisation	NaCl reduction in wastewater and environment	1 \ 2	1 \ 2	1 \ 2	1 \ 2	na	na	na	na	na	1 \ 2	na	na	na	2.0
	Raw hide and skin preservation	Residual NaCl	Preservation of hides with sodium chlorite	NaCl reduction in wastewater and environment	2 \ 2	2 \ 2	2 \ 2	2 \ 2	na	na	na	na	na	2 \ 2	na	na	na	4.0
	Raw hide and skin preservation	Residual NaCl	Recovery and valorisation of residual sodium chloride	NaCl reduction in wastewater and environment	na	2 \ 2	2 \ 2	2 \ 2	na	na	na	na	na	3 \ 2	na	na	na	4.5
	———	———	Classification of hides according to the final product (leather)	Buffing dust and shavings reduction	3* \ 2	3 \ 2	2 \ 2	2 \ 2	na	na	na	na	na	3* \ 2	na	na	na	5.2
	———	———	Adoption of pre-soaking and pre-fleshing operations	BOD, COD and suspended solid reduction in wastewater	3* \ 2	2 \ 2	3 \ 2	1 \ 2	na	na	na	na	na	3 \ 2	na	na	na	4.8
	Unhairing-Liming	Wastewater	Direct recycling of liming floats	Sulphide, organic nitrogen, BOD and COD reduction in wastewater	3 \ 3	3 \ 3	2 \ 3	1 \ 3	na	na	na	na	na	2 \ 3	na	na	na	6.6
		Wastewater	Recovery and valorisation of hair	Reduction of COD, total nitrogen, sulphide and sedimentable solids in wastewater	3 \ 3	1 \ 3	3* \ 3	1 \ 3	na	na	na	na	na	2 \ 3	na	na	na	6.0
		wastewater and atmospheric emissions	Replacement of sodium sulphide by enzymatic and amine treatment	Reduction of sulphide in wastewater and atmospheric H_2S	3* \ 3	3 \ 3	3* \ 3	3* \ 3	na	na	na	na	na	3* \ 3	na	na	na	9.0
		wastewater and atmospheric emissions	Sulphide oxidation during the unhairing and liming operations	Reduction of sulphide in wastewater and atmospheric H_2S	3 \ 3	2 \ 3	2 \ 3	1 \ 3	na	na	na	na	na	1 \ 3	na	na	na	5.4
	Fleshing	fleshings	Flesh valorisation	Fleshings elimination	3* \ 2	3* \ 2	3* \ 2	3* \ 2	na	na	na	na	na	3* \ 2	na	na	na	6.0
Tanning	Deliming	Wastewater	Carbon dioxide deliming	Reduction of ammoniacal nitrogen, COD, cloride and sulphide in wastewater	3 \ 3	2 \ 3	3 \ 3	3 \ 3	na	na	na	na	na	2 \ 3	na	na	na	7.8
		Wastewater	Sulphide oxidation during the deliming operation	Reduction of sulphide in wastewater and atmospheric H_2S	3 \ 2	2 \ 2	2 \ 2	1 \ 2	na	na	na	na	na	1 \ 2	na	na	na	3.6
		Wastewater	Deliming without ammonia products	Reduction of sulphide in wastewater and atmospheric H_2S	3 \ 2	2 \ 2	3 \ 2	3 \ 2	na	na	na	na	na	3 \ 2	na	na	na	5.6
	Pickling	Wastewater	Recycling of pickling floats	Reduction of COD, sulphate and cloride in wastewater	3* \ 3	3* \ 3	2 \ 3	3 \ 3	na	na	na	na	na	3* \ 3	na	na	na	7.8

Figure 3. Waste Minimisation Opportunity Matrix

Stage	Operation	Waste	Minimisation practice	Result	Minimisation Opportunity													Total Value
					Tannery													$\sum_{1}^{n} \frac{A \times B}{n}$
					A	B	C	D	E	F	G	H	I	J	K	L	M	
Tanning	Pickling	Wastewater	Use of non-fumefying acids together with formic and sulphuric acids in the pickling	Reduction of COD, sulphate and cloride in wastewater	3 \ 3	2 \ 3	2 \ 3	2 \ 3	na	na	na	na	na	3 \ 3	na	na	na	7,2
		Wastewater	Use of oxidants in the pickling	Reduction of COD, sulphate and cloride in wastewater	3 \ 3	2 \ 3	2 \ 3	1 \ 3	na	na	na	na	na	1 \ 3	na	na	na	5,4
	—	—	Splitting operation before tanning	Reduction of wastes containing residual chrome	3* \ 2	3* \ 2	3* \ 2	3* \ 2	na	na	na	na	na	3* \ 2	na	na	na	6.0
	.	.	Shaving operation before tanning	Reduction of wastes containing residual chrome	3 \ 3	1 \ 3	2 \ 3	2 \ 3	na	na	na	na	na	2 \ 3	na	na	na	6,0
	—	—	Trimming operation before tanning	Reduction of wastes containing residual chrome	3 \ 3	1 \ 3	2 \ 3	2 \ 3	na	na	na	na	na	2 \ 3	na	na	na	6,0
	Tanning	Wastewater	High exhaustion tanning	Reduction of residual chrome	3* \ 3	3 \ 3	3* \ 3	3 \ 3	na	na	na	na	na	3* \ 3	na	na	na	9,0
		Wastewater	Direct recycling of chrome tanning floats	Reduction of residual chrome	3 \ 3	2 \ 3	2 \ 3	3* \ 3	na	na	na	na	na	1 \ 3	na	na	na	6.6
		Wastewater	Recovery and reuse of residual chrome, through precipitation	Reduction of residual chrome	3 \ 3	3 \ 3	3 \ 3	1 \ 3	na	na	na	na	na	3* \ 3	na	na	na	7.8
		Wastewater	Replacement of chrome,where as possible, by other tanning agents	Reduction of residual chrome	3 \ 3	2 \ 3	1 \ 3	1 \ 3	na	na	na	na	na	2 \ 3	na	na	na	5,4
Dyeing operations	Shaving	Shavings	Valorisation of shavings	Elimination of the disposal of shavings containing chrome	3* \ 3	3 \ 3	2 \ 3	3 \ 3	2 \ 3	2 \ 3	1 \ 3	2 \ 3	3* \ 3	2 \ 3	2 \ 3	3 \ 3	3 \ 3	7.2
		Shavings	Thermo-chemical destruction of shavings to recover chrome	Elimination of the disposal of shavings containing chrome	3 \ 3	2 \ 3	2 \ 3	1 \ 3	2 \ 3	3 \ 3	2 \ 3	3 \ 3	na	2 \ 3	2 \ 3	3 \ 3	2 \ 3	6,8
	Neutralization	Wastewater	Use of acrylic polymers to fix the re-tanning chrome during the neutralization operation	Reduction of residual chrome	3 \ 3	3 \ 3	3* \ 3	3 \ 3	3* \ 3	3 \ 3	2 \ 3	3* \ 3	na	3 \ 3	na	na	na	8.7
	Re-tanning	Wastewater	Accomplishment of a single treatment by mixing re-tanning agents and fatliquoring products	Reduction of total wastewater volume	3 \ 3	3 \ 3	3 \ 3	3 \ 3	3 \ 3	2 \ 3	1 \ 3	3* \ 3	3 \ 3	3 \ 3	2 \ 3	3 \ 3	na	7.4
		Wastewater	High exhaustion re-tanning	Reduction of residual chrome	3* \ 3	3 \ 3	3 \ 3	3 \ 3	3 \ 3	3 \ 3	3 \ 3	3 \ 3	3* \ 3	3* \ 3	3* \ 3	3* \ 3	na	9,0
		Wastewater	Recovery and reuse of residual chrome re-tanning operation, by precipitation	Reduction of residual chrome	na	3 \ 3	1 \ 3	2 \ 3	3 \ 3	2 \ 3	1 \ 3	1 \ 3	na	na	na	1 \ 3	na	5.3
		Wastewater	Replacement of chrome, where possible, by other re-tanning agents	Reduction of residual chrome	3* \ 3	3* \ 3	3* \ 3	3* \ 3	3* \ 3	3* \ 3	3* \ 3	3* \ 3	3* \ 3	3* \ 3	3* \ 3	3* \ 3	na	9.0

Figure 3. Waste Minimisation Opportunity Matrix (continued)

Stage	Operation	Waste	Minimisation practice	Result	Minimisation Opportunity													Total Value $\sum_{i}^{n} \frac{A \times B}{n}$
					Tannery													
					A	B	C	D	E	F	G	H	I	J	K	L	M	
Dyeing operations	Dyeing / fatliquoring	Wastewater	High exhaustion Dyeing	Reduction of COD in wastewater	3* 3	3* 3	3 3	3 3	3 3	3 3	3 3	3* 3	3* 3	3* 3	3* 3	3* 3	3* 3	9,0
		Wastewater	Continuous immersion dyeing	Reduction of COD in wastewater	3 3	2 3	2 3	1 3	1 3	1 3	1 3	1 3	1 3	1 3	1 3	1 3	1 3	3,9
	Drying	Atmospheric emissions	Infra-red drying, in a tunnel	Reduction of emissions from boilers (SO_x, CO, particulates)	1 1	1 1	1 1	1 1	1 1	1 1	1 1	1 1	1 1	1 1	1 1	1 1	1 1	1,0
	Desempoamento	Buffing dust	Valorisation of buffing dust	Reduction of particulates and elimination of buffing dust	3 3	3 3	2 3	3 3	2 3	2 3	1 3	2 3	3 3	1 3	1 3	3 3	3 3	6,7
	Finishing	Atmospheric emissions	Replacement of lacquer in a solvent base by urethane polymers in an aqueous emulsion	Reduction of VOC	3* 1	3* 1	3 1	3* 1	3* 1	3 1	3 1	3* 1	3* 1	3 1	3* 1	3 1	3 1	3,0
	Finishing	Atmospheric emissions	Finishing using roll coating equipment	Reduction of total atmospheric emissions volume	3* 1	2 1	3 1	1 1	2 1	3* 1	1 1	3* 1	3* 1	2 1	3 1	3 1	1 1	2,7
	Finishing	Atmospheric emissions	Use of finishing products on aqueous base	Reduction of VOC	3* 1	3* 1	3* 1	3* 1	3* 1	3* 1	3* 1	3* 1	3* 1	3* 1	3* 1	3* 1	3 1	9,0
Complete Process	------	Solid waste, wastewater and atmospheric emissions	Recovery and valorisation of residual sodium sulphide	Reduction of sulphide in wastewater and atmospheric H_2S	1 2	1 2	1 2	1 2	na	na	na	na	na	1 2	na	na	na	2,0
	------	Solid waste, wastewater and atmospheric emissions	Automation of hide processing	Reduction of total waste volume	2 3	1 3	1 3	1 3	1 3	3* 3	2 3	3 3	2 3	2 3	2 3	2 3	1 3	5,3
	------	Solid waste, wastewater and atmospheric emissions	Planning of water usage	Reduction of total wastewater volume	3 2	3 2	3 2	3 2	3 2	3* 2	3 2	3* 2	3* 2	3 2	3 2	3 2	3 2	6,0
	------	Solid waste, wastewater and atmospheric emissions	Planning of chemical products usage	Reduction of toxicity degree and polluter potential of wastewater	3 3	3 2	3 2	3 2	3 2	3* 2	3 2	3* 2	3 2	3 2	3 2	3 2	3 2	6,0
	------	Solid waste, wastewater and atmospheric emissions	Recovery of gases and particulates with capture equipment	Reduction of total atmospheric emissions volume	3 2	1 2	3* 2	1 2	3* 2	3* 2	3* 2	3* 2	3* 2	1 2	1 2	3* 2	2 2	5,7
	------	Solid waste, wastewater and atmospheric emissions	Reduction of the stocking time of solid wastes	Undetermined benefit	3* ub	3* ub	3* ub	3* ub	3* ub	3* ub	3* ub	3 ub	3 ub	3 ub	3 ub	3 ub	3 ub	------
	------	Solid waste, wastewater and atmospheric emissions	Valorisation of chemical product packing, if feasible	Undetermined benefit	3* ub	3* ub	3* ub	3* ub	3* ub	3* ub	3* ub	3* ub	3* ub	3* ub	3* ub	3* ub	3* ub	------
	------	Solid waste, wastewater and atmospheric emissions	General cleaning and maintenance of machinery, equipment and work environment	Undetermined benefit	3* ub	3 ub	3* ub	3 ub	3 ub	3 ub	3 ub	3* ub	3* ub	3* ub	3 ub	3 ub	3 ub	------
			Total Value	$\sum_{1}^{m} \frac{A \times B}{n}$	7,1	5.7	5,7	5,1	5,8	6.1	4,8	6,1	5,5	5,4	5,1	6,1	4,9	

Figure 3. Waste Minimisation Opportunity Matrix (continued)

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Prediction of inorganic pollutant release from various cement based materials in disposal/utilisation scenario based on the application of a multi-parameter leaching tool box

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The aim of this study is to assess the long term release of contaminants from cement based stabilised wastes. According to the methodology proposed by the European standard ENV 12 920, the impact of waste in disposal/utilisation scenarios has to be evaluated before being exposed to the environment. For this objective we propose a combined experimental and modelling procedure. Firstly a "tool box" consisting of some tests as the Pore Water simulation test (PW), the Maximum Leachable Fraction test (MLF), the Acid Neutralisation Capacity test (ANC), and the Monolithic Leaching Test (MLT) is used to characterise the waste containing material. Secondly the results of the tests are the necessary input parameters for the coupled physico-chemical leaching model that provides the long-term leaching behaviour. For applying the tool box and the model validation, Ordinary Portland Cement with additives was used to prepare the samples containing 25% of binder, 1% of Pb, and sand. The release mechanisms are described. The model provides the long-term release amounts of pollutants as well as the expected concentrations of pollutants in surrounding natural water over several centuries in the considered scenario conditions.

Keywords: Waste Stabilisation, Leaching test, Long-term prediction, Modelling, Diffusion

1. INTRODUCTION

A main economical and environmental objective is to assess or provide a solution for waste disposal and/or its utilisation. The methodology proposed as the European standard "basic characterisation of leaching behaviour in specified conditions" ENV 12 920 [1] consists of several steps some of which inevitably make use leaching tests and environmental behavioural model. Since a great number of leaching tests exist [2], some tests have to be selected in regard to parameter identification for release modelling. We propose a "tool box" consisting of three major tests;

- the Pore Water simulation test (PW) and the Maximum Leachable Fraction test (MLF), designed to determine chemical composition of pore solution and the maximum mobile fraction.
- the Acid Neutralisation Capacity test (ANC), proposed as European pre-standard N 148 aimed to study the pH influence on the release of constituents from a waste material in contact with aqueous solution.

- the Monolithic Leaching Test (MLT), aiming at identifying the pollutant fluxes during leaching process.

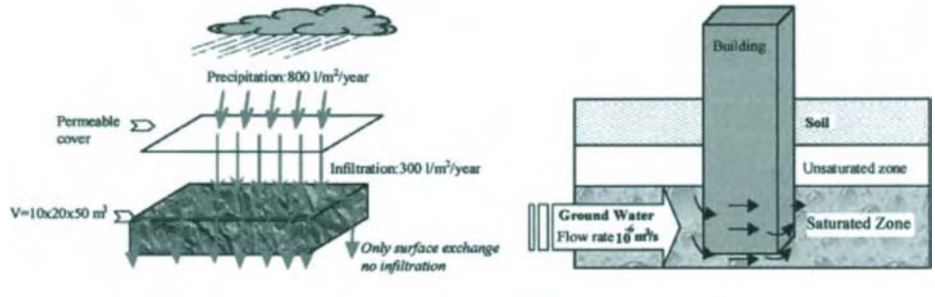
The aim of this study was to demonstrate the application of the leaching "tool box on: (i) the investigation of the pollutant physico-chemical release mechanisms under leaching conditions, (ii) the model parameter identification and (iii) the pollutant long-term release modelling under scenario conditions.

2. SCENARIO DESCRIPTION

Two types of simplified scenario are proposed and defined;

Scenario I: The material is disposed as one monolith with a top cover letting a certain level of infiltration of rain [Figure 1(a)]. The average annual rainfall in France is about 800 l/m^2/year. The monolith is covered by a permeable layer through which rainwater penetrates continuously with an approximate flow rate of 300 l/m^2/year. The deposited stabilised waste is indirectly washed off by rainwater.

Scenario II: An underground wall is in contact with ground water [Figure 1(b)] whose the average flow rate is about 10^{-6} m^3/s.



(a) (b)

Figure 1: Schematic presentation of (a) the landfill and (b) the construction scenario

The composition of both rainwater and ground water is also simplified in that it does not contain any contaminant. We assume that there is neither percolation through the material nor modification of the physical properties and liquid/solid contact characteristics during the simulated time will be 100 years. The mass transfer toward the contact solution is only the leaching from the wet surface of the bloc. Only inorganic pollutants are considered.

3. MATERIALS AND METHODS

3.1 Material and Sample preparation

Ordinary Portland Cement with additives (OPC CEM II) was used to prepare the concrete specimens according to the standard CEN EN 196-1. It contained 25 % of cement, 1.07 % of PbO and sand. The specimens were kept in closed moulds for 28 days. After this curing time, their physical properties were determined: Density = 2222 kg/m^3, Humidity = 6.14 %, Open leaching porosity calculated from Water Absorption Capacity = 18.49 %.

3.2 Laboratory Leaching Tests: "Tool box" description

The proposed leaching tool box comprises three leaching tests. These tests had been developed in order to characterise the main mechanisms of mass transfer during leaching.

Pore Water Simulation (PW) and Maximum Leachable Fraction (MLF) Test

The material was crushed to $\leq$ 1 mm and then put into contact with demineralised water with different Liquid/Solid (L/S) ratios: 200, 100, 50, 10, 2, 1 and 0.3 ml/g (dried material) in polyethylene vessels for 7 days with agitation. The mixtures were filtered through the 0.45 µm filter membrane under nitrogen pressure to avoid the CO_2 uptake. The pH, conductivity, Redox potential were measured. The solutions were analysed.

Acid Neutralisation Capacity Test (ANC)

The test is based on the methodology of characterisation of leaching behaviour (pH influence on the pollutant solubility), known as European pre-standard N 148 [3]. Several test portions of fragmented sample ($\leq$ 1 mm) were put in contact with respective volumes of aqueous solutions (acid and base) with fixed L/S ratio 10 ml/g(dried material) in closed vessels for 7 days at room temperature under agitation. The mixtures were filtered through the 0.45 µm filter membrane. The pH, conductivity, Redox potential were measured. The solutions were analysed afterward.

Monolithic Leaching Test (MLT)

The test was conducted on monolithic cubic specimens (4x4x4 cm^3) with solution renewal at 0.25, 1, 2, 4, 9, 16, 36 and 64 days. The samples were put in demineralised water at Liquid/Surface ratio 10 cm^3/cm^2. Every change of solution, the weighing of samples, the filtration and the measurement of pH, conductivity, Redox potential, and total solid dissolved (TDS) was undertaken as well as the analysis of solutions.

Analyses The solutions were analysed for chloride and sulphate ion by ion chromatography consisting of a Dionex, with conductivity detection. After acidification of the filtrates to pH 2 ± 0.5 with HNO_3 solution (65%), the content of Ca, Na, K, and Pb were determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

4. MODEL DEVELOPMENT AND APPLICATION

The newly proposed leaching model was developed on the basis of solid-liquid reactor with solution renewal (Continuous Stirred Tank Reactor). The model takes into account the coupling of the transport phenomena with the major chemical reactions (dissolution, precipitation, and complexation) of inorganic species. The five major species (Ca, Na, K, Cl, and Pb) are considered.

The parameters used as input values for the behavioural model are identified by the leaching tests contained in the "tool box". The necessary parameters for modelling are (i) the initial concentration of each soluble species in the pore solution (ii) the initial concentration of each solid phase and (iii) the effective diffusion coefficients of relevant mobile species obtained by adjustment of the simulation results to the experimental data of Tank Leach Test and (iv) the equilibrium constants from the ANC data.

5. RESULTS AND DISCUSSION

Pore Water Simulation (PW) and Maximum Leachable Fraction (MLF) Test: The results of the test is shown in Figure 2. The high concentrations of sodium and potassium in the pore solution confirm that the pH of cement pore solution is mainly controlled by dissolved alkaline ions. Whereas the concentration of calcium depends on the concentration of sodium and potassium. It is limited by the solubility constant of Portlandite [7]. The pore water amount in the cement matrix (L/S) can be evaluated from the Water Absorption Capacity determined from Monolithic Leaching Test. We can extrapolate the curves of the element concentrations toward the L/S of pore water. The initial concentrations of every species in the pore solution are estimated and introduced in the model (input values).

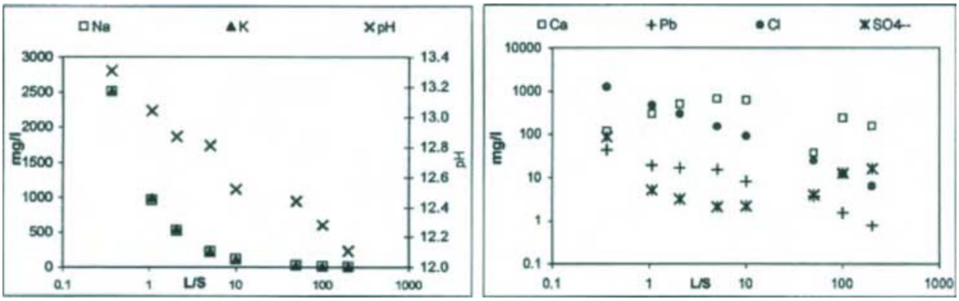


Figure 2 : pH and concentration of relevant species in the pore solution

The leachable amount of each element can be estimated from the extrapolation of the extracted quantities in mg/kg toward the infinite L/S (see Figure 3). We can then convert into pore concentration in solid phase (input parameters of the model).

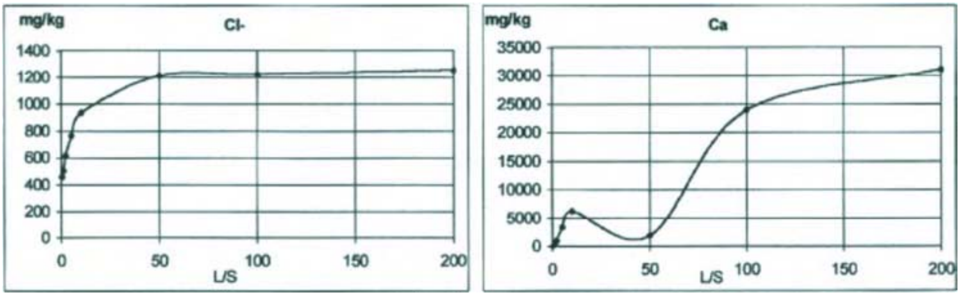


Figure 3 : Extracted quantities in mg/kg of chloride and calcium

Acid Neutralisation Capacity Test (ANC) : The influence of pH on the solubility of lead is shown in Figure 4-left. Due to the unknown chemical speciation of solid phases of lead in the cement matrix, we determine the Pb solubility in the pore solution by regression of the pH solubility curve instead of the solubility constant of $Pb(OH)_2$, which will soon be introduced in the model.

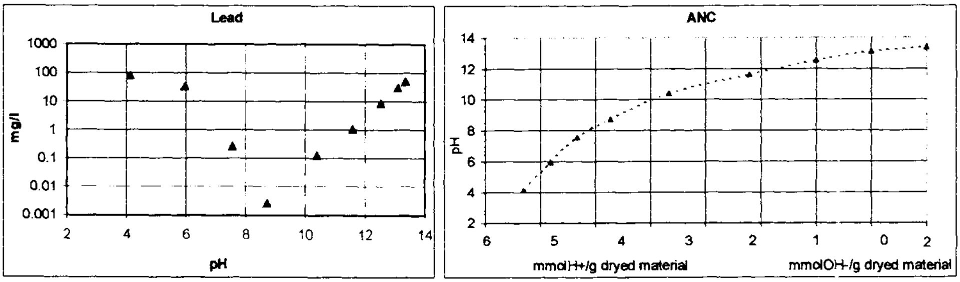


Figure 4 : Concentration of lead in function of pH and ANC of the samples

Monolithic Leaching Test (MLT) : The pH of the leachate (see Figure 5) remained virtually constant during the test. The pH is controlled by leaching of soluble species from the cement matrix, mainly alkaline species, Portlandite, and CSH. Mass balance were performed based on the initial sample mass of the test and after 64 days of leaching, and on the calculated masses lost by leaching. The water absorption capacity or the amounts of water adsorbed by the samples roughly correspond to the amounts required to saturate the pores.

Simulation results: The effective diffusion coefficients of each species are evaluated by the best consistency of simulation results and experimental ones. The simulation and the experimental results are compared in Figure 5. The pH and calculated average flux of relevant species in *mmol/m^{2}s* are plotted against mean square root of time (T_i in days).

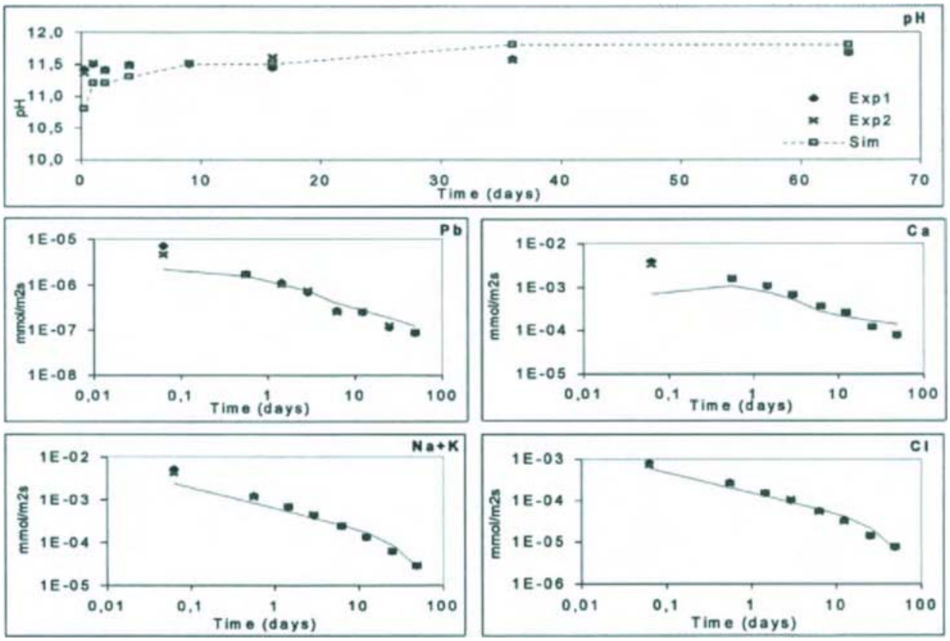
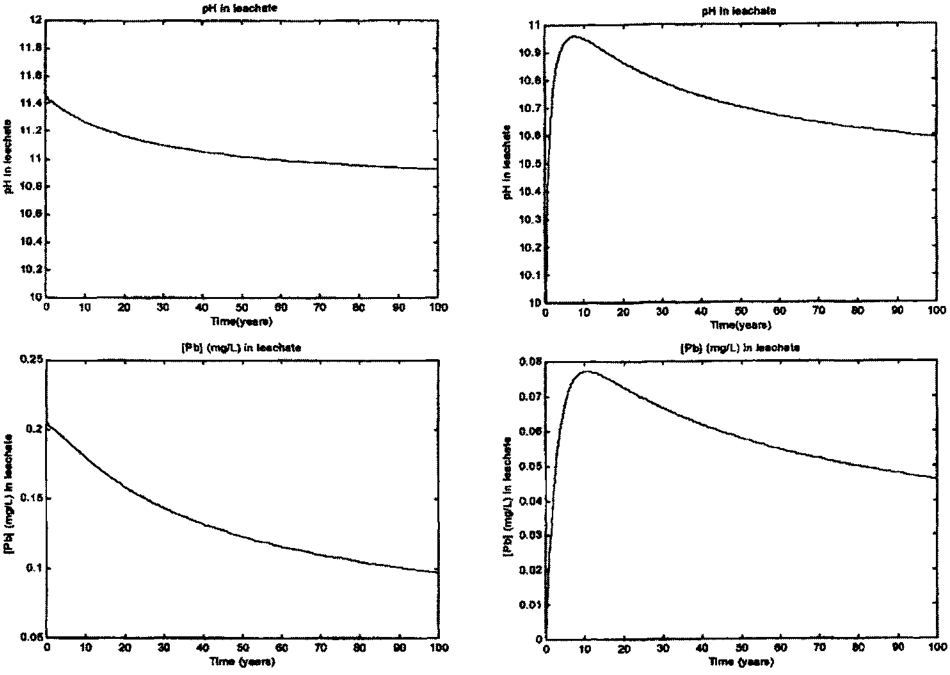


Figure 5: Experimental and simulation pH and considered species flux

We observe that the simulation values of the pH and the flux reproduce very well the experimental values, although initial surfaces wash-off phenomena were found to control the rate of release during the first few days of the leaching period. The simulated pH is a global parameter of the leaching system because it is calculated from the thermodynamic equilibrium condition of the pore solution and leachate. This shows the performance of the proposed coupled physico-chemical model in the description of the leaching results. On this basis, more realistic prediction can be proposed.

6. PREDICTION IN DISPOSAL/UTILISATION SCENARIO

The calculation programme needs the scenario parameters as defined previously: the flow rates of effective rainwater (300 $l/m^2/year$) and ground water (1.10^{-6} m^3/s), the chemical composition of rainwater, and the dimension of the monolithic bloc. The simulation has been done over 100 years. The model can provide the concentration and the cumulative released amount of each species in leachate. The prediction of pH and pollutant release (Pb) is proposed in Figure 6.



(a) Scenario I (b) Scenario II

Figure 6: Scenario simulated concentration of Pb in the leachate

We can also provide the prediction of other relevant species. These values can be compared for example with the acceptability limit for drinking water. In this respect, we could answer if the material under the scenarios is accepted in relation to environment assessment.

7. CONCLUSIONS AND PERSPECTIVE

The objective of this research project was the proposal of a multi-parameter leaching "tool box" for the determination of the parameter controlling the release of pollutant from the stabilised wastes and the development of leaching model. The developed model describes more correctly the leaching phenomena. The necessary input parameters are obtained from the leaching tests composing the "tool box". They are assembled in Table 1.

Table 1: Model input parameters identification from the "tool box"

Input parameters	Test
Physical properties of specimen	Monolithic Leaching Test
Equilibrium constants	Literature and Acid Neutralisation Test
Initial concentrations in pore solution	Pore Water Simulation Test
Leachable quantities	Maximum Leachable Fraction Test and Acid Neutralisation Test

These approach can be applied to various cement based stabilised wastes. There is evidence that the application of the "tool box" and the use of the new physico-chemical leaching model are sufficiently consistent for predicting the environmental behaviour of released pollutants. The model computational programme can be modified for specific considered scenarios for example the landfill and utilisation as construction material.

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Recycling Options for Gypsum from Construction and Demolition Waste

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Waste gypsum from the construction materials sector is an important part of the construction and demolition waste (CDW). Although pure gypsum can be recycled infinitely, impure waste gypsum is often disposed of or dispersed in the CDW stream. Source separation is not performed on a large scale and sorting units for CDW often do not perform a gypsum selection. The sulphate content is a major criterion in the valorisation of the CDW as a secondary aggregate for concrete. Therefore, the question arises whether the presence of residual gypsum in CDW masonry aggregates is a burden for effective valorisation.
The actual gypsum content and sulphate leachability was studied for a range of sorted and recycled aggregates. This was compared to the overall environmental quality of the material. Visual analysis of the various products from sorting and recycling gave data on the gypsum content. On this basis a material flow diagram of gypsum is set up. This allows to determine the gypsum recycling potential on the Flemish market. In order to optimise gypsum recycling from CDW, source selection measures need to be taken and a centralised collection and treatment system needs to be set up.

1. INTRODUCTION

Construction and demolition waste (CDW) is one of the main non-municipal waste streams, with a yearly production of about 5 million tons in Flanders. This equals about 800 kg per citizen every year. The Flemish Government has defined a sectoral implementation strategy for construction and demolition waste (CDW). This implies a maximisation of the valorisation, the aim is to reuse at least 75% of the CDW by the year 2000. In order to reach this goal, the valorisation options for specific parts of the CDW, such as gypsum needs to be known. Setting up a substance flow analysis of the material allows assessment of recycling options.

Recycling units process CDW in a primarily mechanical way. They work under a strict quality policy and produce aggregates with certified quality. The recycling units perform a strict acceptation control on the incoming material. The absence of waste gypsum is one of the main criteria. Loads having more than 1% of gypsum are not accepted. At the production side, the absence of gypsum in the produced aggregate is monitored through regular sampling.

The end product has a good environmental and technical quality, and is valorised as a secondary raw material.[1]

Sorting units process the mixed CDW streams. They perform a manual or partially mechanical separation. This separation aims at removing metals, plastics, glass and wood. Separation of gypsum was not performed until recently, because a driving force has been lacking. The sorting units produce a sand fraction and one or more aggregates. These are sold as construction and filler sand.

Rubble aggregates and sorting fractions are valorised as a secondary construction material. They must comply with environmental criteria defined in VLAREA (Flemish Regulation on Waste Prevention and Management). The secondary material is used as filling sand in noise abatement walls, dikes, parkings,...and as a road base material. The presence of gypsum has a negative effect on the material quality for reasons of solubility and low hardness and density. The grain strength of broken gypsum product is too low for application as coarse additive in lean concrete.[2] Additionally gypsum affects the hardening reactions during concrete production. Therefore, the sulphate content is a major criterion in the valorisation of the CDW as a secondary aggregate. The question arises whether the presence of residual gypsum in CDW masonry aggregates is a burden for effective valorisation.

Waste gypsum can be recycled to new gypsum products through a cycle of calcination and rehydration. When performed at the gypsum product manufacturer, this process requires a relatively pure starting material. Recycling of polluted gypsum products is performed in specialised plants. These produce gypsum anhydrite or apply the gypsum as a raw material in cement and sulphuric acid production. Setting up an effective recycling system requires a good collection, separation and transport infrastructure. This can only be done in an economical way for sufficient quantities of waste material.

In this study a substance flow of waste gypsum is set up for Flanders and the effect of gypsum on aggregate quality is studied. From these data the driving forces and possible impediments for implementation of a gypsum recycling system can be defined.

2. SUBSTANCE FLOW ANALYSIS

2.1. Construction and Demolition Waste

In order to gain insight in the availability of gypsum for recycling, the gypsum cycle as it exists today is set out. Inventory data from the sector and sampling at selected recycling and sorting units allowed us to set up the material cycle presented in Figure 1. This gives the situation for Flanders in 1997. The line thickness refers to the relative presence of gypsum in the waste stream.

The gypsum product producers delivered 411 kton material at the construction market. These are plasters (48%), wall board (43%) and blocks (9%). Part of the production goes to industrial users. The production residue and residue from the industrial users is a relatively clean material, that can be recycled in the production of new wallboard. The industrial users can provide a potential flow of 0.425 kton of this clean residue. This material should be prevented from ending up in the waste circuit, since a high grade valorisation route exists.

The gypsum products are applied as a construction material (primary use) and end up as part of the construction and demolition waste stream. The total amount of construction and demolition waste (CDW) in Flanders in 1997 amounted to 4700 kton. The CDW is composed of 41% concrete rubble, 40% masonry and 12% asphalt. The remainder is a mix of gypsum, ceramics, wood, roof tiles, metals, glass,...[3] Through logistical services, this material finds 3 destinations: sorting units, recycling units and the category 3 disposal site.

An inventory of part of the sorting sector was made up with the co-operation of VSO (Flemish Sorting Organisation). This is a sectorial organisation of small and medium sized sorting units. The members all have both collection and sorting activities. 75% of the VSO members returned an enquiry on their 1997 production. The data have been extrapolated accordingly.

VSO treats 545 kton CDW, primarily masonry rubble, being 12% of the total CDW flow. The rest fraction (plastics, furniture, glass, wood,...) is disposed at category 2 sites. 200 kton sorted debris were reused as (course or fine) secondary material. 233 kton stony material was brought to recycling units for further upgrading to secondary aggregates.

The total flow of CDW to the recycling units is estimated at 3000 kton. This includes asphalt and concrete from road and infrastructural works. The Flemish category 3 disposal sites acquired 174 kton CDW in 1997. The figure shows that the destination of 1000 kton of waste remains uncertain. This will be mainly in the circuit of waste collection and export.

2.2. Gypsum in CDW

In order to complete the substance flow diagram with data on gypsum flows, an experimental study was performed. Sand and aggregate products both from recycling units and sorting plants were taken and submitted to visual analysis and environmental characterisation. Samples were taken at 9 recycling units and 5 sorting plants. In total 32 different materials were tested.

For visual analysis each sample is sieved into various fractions. The composition of each fraction is determined visually. For the particles <4mm a stereomicroscope is used. This allowed to determine the gypsum content for each material.

The gypsum content of recycled aggregates varies form 0.03%m/m in concrete rubble to more than 3%m/m in some sieving sands. The gypsum occurs in finely dispersed form and originates mainly from plaster work. Due to the low levels and the fine dispersion a high gain recycling appears unfeasible.

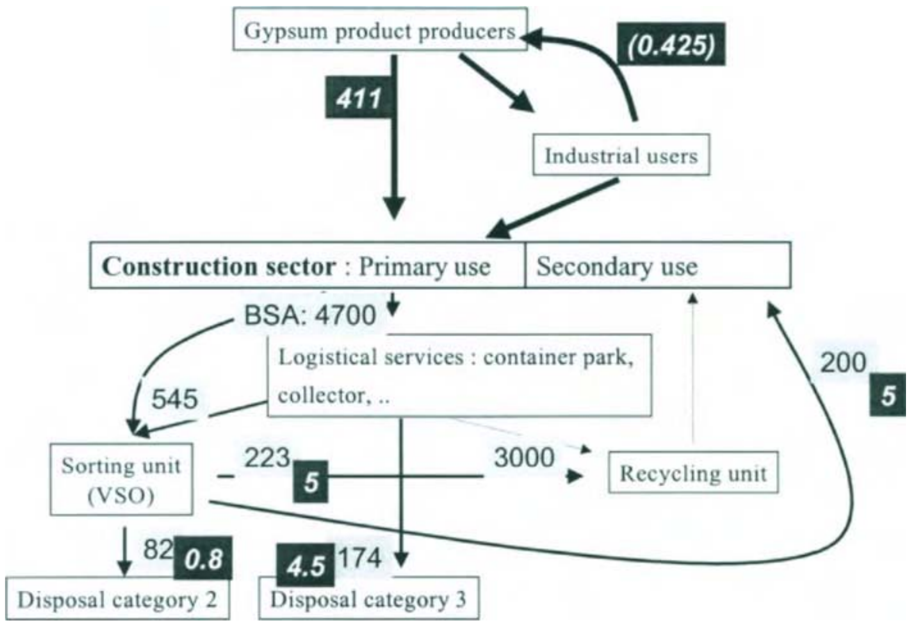

Figure 1 : Material flow through the gypsum and CDW sector, data in kton/j, for 1997, CDW and aggregates (incl. gypsum) , *gypsum*

The gypsum content in sorting unit products varies from 0.5%m/m to 5% m/m. The average gypsum content in the investigated material is 2.6% m/m. This percentage was used for further calculation of the amount of the gypsum substance flow analysis. The resulting figures are given in Figure 1. If the material for disposal is accounted for, together with the sorted flow, the total traceable flow of gypsum in construction and demolition waste amounts up to 15.5 kton/y.

This gypsum has the form of broken and impure wall boards, blocks and plaster work. A Dutch study states that a separation rate of 30% can be achieved for gypsum in a sorting unit.[4] This holds for a system with mechanical pre-screening, followed by handpicking. An optimised gypsum selection of the present traceable CDW flow, by separation at the sorting unit would therefore result in some 3.300 ton gypsum on a yearly basis. Source separation, however, would result in much higher recovery rates and a much cleaner product. Vroonhof reports recovery rates of up to 95%.[4]

In order to optimise gypsum recycling from CDW, source selection measures need to be taken. On basis of current calculations this may yield more than 10.000 ton of gypsum per year.

3. SULPHATE LEACHING

Besides visual inspection, an environmental characterisation of the sand and aggregate fractions was performed as well. Sulphate leaching was measured using two-step leaching tests following prEN12457-3. This is a batch mixing test in which the material is leached with demineralised water, consecutively at L/S = 2 l/kg and L/S = 8 l/kg. The resulting leaching value is added up to a cumulative release at L/S = 10l/kg. The results are given in Figure 2.

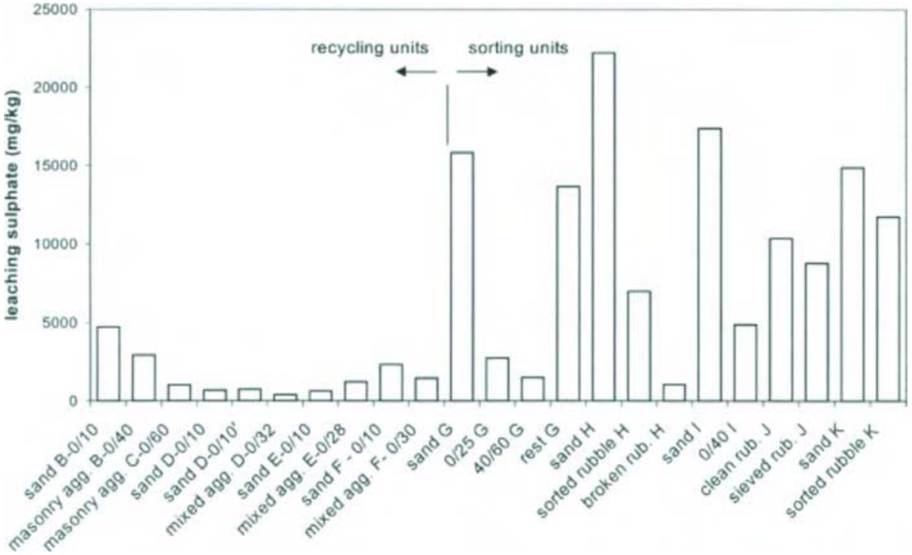

Figure 2 : sulphate leaching (in mg/kg, following prEN12457-3) from sand and aggregate fractions: A-F recycling units; G-K sorting units

A major difference exists between products from sorting and recycling units. Recycled aggregates show a sulphate leaching level between 390 and 4700 mg/kg. For a selected plant, the sand fraction generally has a higher sulphate leaching than the aggregates. The sulphate shows a fast initial leaching. The maximal solubility level is not reached.

Sulphate leaching for sorting product is at a much higher level. Values vary between 1500 and 22000 mg/kg. Comparison according to the material type shows that sulphate leaching is always higher for the finer material. Additionally, clear difference occurs between the various units. Plants with a wind sifter generate an aggregate with lower sulphate leaching, as compared to plants without this type of separation. Also the amount of mechanical separation lowers sulphate leaching of the coarse factions. Plants that only have manual sorting (J, K) produce material with high sulphate leaching.

Evaluation of the leaching values in both steps of the two-step test gives information on the leaching mechanism. For the coarse fractions, leaching is initially controlled by the solubility of calcium sulphate. In the second step depletion is the controlling mechanism. For the sand fractions from the sorting units, the leaching is solubility controlled in both steps. The gypsum content of the sand fractions is estimated visually at a few percents (>5%). The cumulative emission is in the range of 15-20 g/kg. This value equals the leaching measured on pure gypsum products. Due to the solubility controlled leaching mechanism, the material with a gypsum content of a few percents (>5%) shows an identical sulphate emission as pure gypsum products.

4. THE EFFECT OF GYPSUM ON AGGREGATE QUALITY

The results reported above, show that gypsum construction materials are mainly found back in masonry aggregates and sands, processed by sorting units. The aggregates show a sulphate content of 2.6%m/m. Sieving sands have a higher gypsum content and a sulphate leaching level of 15-20 g/kg. The question arises whether this presence of residual gypsum in CDW masonry aggregates is a burden for effective valorisation.

Toxicological data for man, fauna and flora show that sulphates have a very minor toxicity. For this reason, the Flemish legislation currently has no leaching limit value for sulphate leaching from secondary construction materials. The possible risk of sulphate leaching is an increase of the sulphate level in ground and drinking water. The World Health Organisation mentions a level of 250 mg/l sulphate in drinking water a 'likely to give rise to consumer complaints'.[5] This is due to possible changes in taste and possible corrosion of piping. A correlation scenario between sulphate emission from construction materials and drinking water quality is currently worked out. Thus, the presence of gypsum in the secondary construction material is no burden for valorisation in the context of the current Flemish environmental legislation.

The presence of gypsum in secondary aggregates does have an effect on the technical quality of the material. Due to its solubility, its low hardness and low density gypsum has a negative effect on aggregate quality. These properties prevent the use of gypsum containing products as unbound elevation or foundation material. In cement bound applications, an excess of sulphates causes loss of strength, expansion and disintegration of concrete. The maximal amount of soluble sulphates is limited in various national and European standards. the European pre-standards, that are set up on CEN-level (e.g. prEN 12620[6] and prEN 13242[7]), define maximal levels of soluble sulphates of 0.2%, 0.8% and 1.0%.

5. SELECTION AND VALORISATION OF GYPSUM FROM CDW

Selection of gypsum from CDW should be performed for mainly technical reasons. An optimal recovery rate can be obtained with source separation measures. Thus, the material does not get finely dispersed in the CDW flow. For the Flemish market, the effective recycling of gypsum from CDW is mainly a question of logistics. Until recently no system of collection of gypsum waste existed. The recycling of impure gypsum can only be performed in industrial units abroad (mainly Germany). In view of the relatively small amount of gypsum in the CDW cycle, a centralised collection and transportation system is essential. Setting up a working gypsum recycling system will therefore involve co-operation of building contractors, the sorting sector, the gypsum industry and the Government. An economical evaluation should prove the feasibility of this treatment system.

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Analysis of Literature Data from 3,000 Cement/Waste Products

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In the last two decades, a large amount of references regarding cement/waste systems have been published. The information reported in these references has been focused on two main topics: inertization of wastes using cementitious materials as binders through solidification/stabilization techniques (typically low binder dosages), and reutilization of non hazardous wastes after mixing with cementitious materials (typically low waste dosages).

The information contained in near 3,000 cement/waste products collected in a previous work in an Access database has been evaluated according to the following points: level of identification of composition of products (types of components in product formulation – waste, non-waste materials, and water-, elemental and oxides composition of components and physical properties of components), physical and mechanical properties of products, and leaching tests (types of tests and chemistry of the leachate of waste and products).

Wastes have been classified according to the European Waste Catalogue (EWC). From the studied data, it can be found a certain lack of information on the formulations of the products (e.g. water content is not given in 28 % of products). With respect to engineering properties, unconfined compressive strength is reported in 70 % of products; nevertheless, very few data for setting time have been found (3-4 % of the products).

The main leaching tests performed to wastes and products are European (DIN 38414-S4) and US (USEPA EP-tox and TCLP) standard tests and the main elements measured in the leachate are As, Ca, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn.

Conclusions related to the difficulties, which have been found in the literature data to get a useful description of cement/waste mixings, mechanical properties and environmental behaviour will be explained.

1. INTRODUCTION

The use of cementitious materials in waste management has been widely studied in the last decades, in solidification/stabilization technologies previous to landfilling (as a binder material), and in reutilization of some specific wastes (as building materials).

A collection of several hundreds of cement/waste products reported in the recent literature regarding both topics, inertization and reutilization of wastes, has been performed in the context of the project "Neural Network Analysis for Prediction of Interactions in Cement/Waste Systems". References containing information from more than 50 cement/waste products are shown in 'References' section [1-10]. The collection of data was based on a literature search previously preformed [11]. All data have been entered in a database called "Cement/waste systems database" developed for this purpose by Buckley and Johnston [12].

The aim of this work is to evaluate the information of the series of cement/waste systems data contained in this database. In summary, it contains 2965 cement/waste products from 108 references; 68 different types of wastes, according to the European Waste Catalogue, are included in their formulation.

Different sets of tables showing the type of information contained in the database will be presented, but only including the most numerous records.

2. EVALUATION OF DATA

A complete description of a cement/waste product should include the chemical and physical characteristics of all the wastes and cementitious materials constituting the product, a clear definition of the formulation of the product, and the physical and environmental (through leaching tests) behaviour of the products.

Taking into account these principles, the information contained in 3000 cement/waste products has been evaluated according to the following subjects:

- level of identification of components and products
- physical and mechanical properties of products
- leaching tests of components and products

2.1. Evaluation of the level of identification of components and products

When analyzing the level of identification of components and products, the following questions can be stated:

Which are the typical components in product formulation and how well defined is the formulation of the mix? and, which are the main variables describing the components?

These questions have been asked to the database.

2.1.1. Types of components in product formulation

Components are defined as each of the constituents in product formulations: they can be wastes (including residual binders) or non-waste materials, as commercial binders, aggregates, admixtures and additives.

From the 2965 cement/waste products, the main types of wastes included in product formulation are shown in Table 1 and 2, according to the classification of the European Waste Catalogue. This Catalogue applies to all wastes, irrespective of whether they are destined for disposal or for recovery operations. However, the inclusion of a material in the EWC does not mean that the material is a waste in all circumstances, but it should constitute the basic reference for the Community Programme on waste statistics.

The catalogue classifies the wastes in 20 main categories (XX 00 00); inside each main category, there are subcategories with the format (XX XX 00); finally, each type of waste inside the subcategories has an individual code of waste (XX XX XX), but this code should not be isolated from its heading. For example, the code 10 00 00 corresponds to inorganic wastes from thermal processes, 10 01 00 to wastes from power station and other combustion plants (except 19 00 00), and 10 01 02 to coal fly ash.

Table 1 shows the number of products containing each type of waste (the percentage with respect to the total number of products is also given in parentheses), according to the first two digits of the code (it corresponds to the main categories of wastes), and Table 2, according to the individual code (6 digits).

Table 1. Types of wastes in product formulation (EWC, 2 digits)

EWC	Number of products	Description
01	57 (1.9 %)	waste resulting from exploration, mining, dressing and further treatment of minerals and quarrying
02	11 (<1 %)	waste from agricultural, horticultural, hunting, fishing and aquaculture primary production, food preparation and processing
03	30 (1.0 %)	wastes from wood processing and the production of paper, cardboard, pulp, panels and furniture
04	23 (<1 %)	wastes from the leather and textile industries
05	1 (<1 %)	wastes from petroleum refining, natural gas purification and pyrolytic treatment of coal
06	333 (11 %)	wastes from inorganic chemical processes
07	91 (3.1 %)	wastes from organic chemical processes
08	22 (<1 %)	wastes from the manufacture, formulation, supply and use (MFSU) of coatings, (paints, varnishes and vitreous enamels), adhesive, sealants and printing inks
10	1630 (55 %)	inorganic wastes from thermal processes
11	250 (8.4 %)	inorganic waste with metals from metal treatment and the coating of metals; non-ferrous hydrometallurgy
12	2 (<1 %)	wastes from shaping and surface treatment of metals and plastics
13	4 (<1 %)	oil wastes (except edible oils, 05 00 00 and 12 00 00)
14	9 (<1 %)	wastes from organic substances employed as solvents (except 07 00 00 and 08 00 00)
16	155 (5.2 %)	waste not otherwise specified in the catalogue
17	23 (<1 %)	construction and demolition waste (including road construction)
19	898 (30 %)	wastes from waste treatment facilities, off-site waste water treatment plants and the water industry
20	6 (<1 %)	municipal wastes and similar commercial, industrial and institutional wastes including separately collected fractions

Table 2. Types of wastes in product formulation (EWC, 6 digits)

EWC	Number of products	Waste description
06 04 03	70 (2.4 %)	wastes containing arsenic
07 00 00	63 (2.1 %)	wastes from organic chemical processes
10 01 02	1043 (35 %)	coal fly ash
10 02 02	218 (7.4 %)	unprocessed slag
10 08 05	156 (5.3 %)	solid waste from gas treatment
11 01 03	144 (4.9 %)	cyanide-free wastes containing chromium
11 01 04	84 (2.8 %)	cyanide-free wastes not containing chromium
16 00 00	154 (5.2 %)	waste not otherwise specified in the catalogue
19 01 03	782 (26 %)	fly ash
19 08 00	57 (1.9 %)	wastes from waste water treatment plants not otherwise specified

Table 3. Types of non-waste materials in product formulation

BINDER/AGGREGATE/ADDITIVE	Number of products
Aggregate	305 (10 %)
Another additives	158 (5.3 %)
Another pozzolan	119 (4.0 %)
Clay	288 (9.7 %)
Coarse aggregate	372 (13 %)
Fine aggregate	610 (21 %)
Gypsum	164 (5.5 %)
Hydrated Lime	520 (18 %)
Plasticiser	237 (8.0 %)
Portland Cement	470 (16 %)
Portland Cement Type I (10)	1824 (62 %)
Portland Cement Type III (30)	170 (5.7 %)
Sand	220 (7.4 %)
White cement	129 (4.3 %)

The other constituents in product formulation are lumped as non-waste materials (commercial binders, aggregates, admixtures and additives). A list of non-waste materials is shown in Table 3. It includes the number of products which contain each type of non-waste material.

Water content in product formulation is a very important parameter that affects the properties of the final cement/waste product. It can be reported as added water or total water. Table 4 shows the number of products where water is reported as one of the components of the product.

2.1.2. Product formulation

To evaluate the quality of the formulation of cement/waste products, all components were initially classified into three main groups: waste material (including real wastes, synthetic wastes, and binder type wastes), non-waste material (including commercial binders, additives, admixtures and aggregates), and water (which was sometimes expressed as added, sometimes as total water).

Three separate crossed queries were prepared in order to sum the composition of all the components of each group for every product. Once these initial queries were performed, a new query was designed containing the product identification (code for the identification of each product), the % of waste material, the % of non-waste material, the sum of waste and non-waste material, and the % of added or total water.

Table 4. Water in product formulation

WATER	Number of products
Added water	1102 (37 %)
Total water	1358 (46 %)

The units for the composition of each component were defined as 'dry weight % of total dry mix'; therefore, the sum of the composition of the dry fraction of the waste and non-waste solid material must be 100 %. From the total number of products, 2965, and after applying the queries for checking the quality of product formulations, it can be presented the following remarks:

- There are 221 products where the formulation is unknown or not given in appropriate units.
- From the 2774 products where the units of the composition have been transformed to 'dry weight % of total dry mix', 2626 show a composition of 100 % (between 99.5 and 100.5).
- The percentage of aggregate was not given in some of these products. However, the percentage sums 100 % because the calculation basis in these products does not include aggregates (i.e., information about the aggregate content was omitted from the reference).
- With respect to the water content, from the total number of products (2965), 839 products do not report this value. Then, 2126 products show the water content.
- From the 2774 products where the units of the composition have been transformed to 'dry weight % of total dry mix', 2094 show the water content.
- From the 2626 products where the formulation sums 100 % in dry basis, 2004 show the water content. Then, there are 2004 products where a full description of the formulation is reported.

2.1.3. Elemental composition of components and products

Elemental composition of wastes can be related to the behaviour of the cement/waste products. The elements contained in wastes can be considered as impurities of cement, modifying its setting and strength. Impurities can cause acceleration or false set (lower setting time) and increase early strength, but can also interfere with microstructure and ultimate strength development, and may increase water demand. Other impurities can act as retarders, decreasing the water demand, and increasing the setting time and workability, but may also affect the strength and durability.

Elemental composition of components is not very often reported in the literature when cement/waste systems are analysed. Elemental composition of products is usually followed through the leachate.

Organic compounds and inorganic anions are even less reported in the studied literature and have not been included in this analysis.

Table 5. Elements determined in components and products

Element	Number of components	Number of products	Element	Number of components	Number of products
Al	51	15	Fe	62	19
As	58	35	Hg	32	22
Ca	51	18	Mg	40	18
Cd	87	35	Mn	43	19
Co	37	30	Ni	74	36
Cr	88	41	Pb	102	39
Cu	69	37	Zn	76	39

Table 6. Oxides composition and inorganic compounds in components

Name of compound	Number of products	Name of compound	Number of products
Al_2O_3	138	Phase C2S	13
CaO	146	Phase C3A	17
Fe_2O_3	133	Phase C3S	14
K_2O	70	Phase C4AF	14
MgO	135	SiO_2	164
Na_2O	73	SO_3	110
P_2O_5	28	TiO_2	33

2.1.4. Oxides composition of components

Oxides composition of components is usually given in portland cements and other commercial binders; it is sometimes reported in residual binders, such as coal fly ash, silica fume and blast furnace slag, where the percentage of the three main oxides, SiO_2, CaO and Al_2O_3 is very important for the behaviour of these materials as binders.

A summary of the types of oxides reported in the literature and the number of components where these oxides are determined is shown in table 6. It also includes phase composition (typically reported in cements).

2.1.5. Other variables

Other characteristic parameters measured in components and products can be mentioned: pH, LOI, and specific surface area.

2.2. Physical and mechanical properties of products

A large number of references reports information regarding physical and mechanical properties in products. A list of these properties given in the studied literature is shown in Table 8; this table also includes the number of products where these properties are measured and the number of records of each property (the number of records is higher than the number of products when the property is measured at different sample ages, or when there are some replicates of the same property).

These properties are usually reported when non-hazardous wastes showing pozzolanic behaviour are blended with cement; some of these wastes are used as additions for portland cement type II and III, as coal fly ash, granulated blast furnace slag or silica fume. However, the characteristics and the maximum amount of these additions are limited. In the literature, a large variety of formulations using these types of wastes can be found, showing strength and other engineering data.

Table 7. General variables of components and products

Name of parameter	Number of components	Number of products
Loss on Ignition	205	0
pH	33	471
Specific Surface area	43	0

Physical and mechanical data are less reported when hazardous wastes are stabilized and/or solidified. In some cases, final products are granular (they do not show any setting and strength properties); in other products, only the leaching behaviour of final cement/waste products is studied.

Table 8. Physical and mechanical properties in products

Property	Age	Count	Total	Number of products
Bulk Density	Not given	200	786	759
	14 days	96		
	24 hours	152		
	28 days	24		
	72 hours	153		
	168 hours	73		
	504 hours	73		
Flexural strength	Not given	10	61	26
	3 days	14		
	7 days	10		
	28 days	16		
	28 days	59		
Porosity	Not given	24	171	115
	14 days	22		
	28 days	51		
	90 days	25		
	365 days	25		
Shrinkage/Expansion	Not given	64	219	134
	10 days	16		
	30 days	14		
	56 days	24		
	72 weeks	25		
	100 days	15		
	200 days	16		
	360 days	14		
Specific Gravity	14 days	90	573	573
	24 hours	146		
	29 days	18		
	72 hours	148		
	168 hours	73		
	504 hours	71		
	56 days	24		

Table 8 (Continuation). Physical and mechanical properties in products

Property	Age	Count	Total	Number of products
Tensile Splitting Strength	28 days	33	57	27
Unconfined Compressive Strength	Not given	71	4116	2088
	1 days	277		
	2 days	12		
	3 days	332		
	6 months	149		
	7 days	569		
	8 days	84		
	14 days	287		
	21 days	98		
	28 days	1157		
	29 days	106		
	35 days	61		
	38 days	75		
	56 days	176		
	90 days	252		
	180 days	30		
	365 days	128		
Initial setting time			108	108
Final setting time			121	121
Slump			201	201

From these properties, unconfined compressive strength (UCS) is the most determined variable: 4116 records (2088 products where UCS is measured); it is measured in 28 days aged samples (1157 records), following by 7 days (569 records), 3 days (332 records), 14 days (287 records), 1 day (277 records), 90 days (252 records), 56 days (176 records), and 365 days (128 records).

The setting of the cement/waste products should be a very important parameter for the possible reutilization of the waste as construction material. However, there are only 108 products that report the initial setting time, and 121 the final setting time (3.6-4.1 %). Other properties also reported are: bulk density, flexural strength, hydraulic conductivity, porosity, shrinkage/expansion and slump.

2.3. Leaching tests

A large information of leaching test in cement/waste products is reported in the literature. However, there is less information of leaching tests in wastes (components in general), when cement/waste systems are studied. Some references only focus on the waste characterization and the leachate chemistry, but they do not report cement/waste mixings.

Leaching tests play an important role in the characterization of the untreated and treated wastes in relation to the actual and potential environmental impacts. From the different types of leaching tests reported in the literature, only single batch extraction tests have been considered in the database.

2.3.1. Types of leaching tests

The different leaching tests (single batch extraction tests) given in the studied literature are shown in Table 9, reporting the number of components (usually wastes) and the number of products where each leaching test is performed.

From leachates, elements and conventional parameters as pH or conductivity are usually measured. The properties of the leachant are not reported very often because of the usual use of standard methods of single batch extraction tests, where these parameters are known.

European (DIN 38414 S4) and US's (USEPA EP-tox and TCLP) standard tests are the most used tests; in addition, many non-standard distilled water extraction are reported. In recent years, acid neutralization capacity tests have also been performed to untreated and treated wastes; it does not constitute a regulatory basis, however, it shows a very valuable information with respect to the mobility of metals under different pH and the resistance of the matrix to acid attack.

2.3.2. Elemental composition in the leachate of components and products

Elemental composition of the leachate of wastes can be carried out as a measure of its toxicity with respect to the environment, and as a method of characterization in order to classify the waste according to its potential hazardous behaviour; sometimes, it is also measured in commercial materials as a reference.

However, from the total number of wastes contained in the database, the information of leachate chemistry is poorer than expected.

Elemental composition of leachant is not measured in the studied literature.

The number of records of the elements typically measured in the leachate is shown in Table 10. The number of components and products where these parameters are measured are shown in parentheses. Different leaching tests can be applied to each waste or product. Moreover, elements can be determined at different pH, and in the case of products, at different sample ages. Therefore, several records of each element can be obtained for the same waste or product.

Table 9. Leaching tests in components and products

Single Batch Extraction Tests	Number of components	Number of products	Total
Acid Neutralization Capacity	17	36	53
ASTM D3987	14	17	31
DIN 38414 S4	12	155	167
Other distilled water extraction	9	135	144
UNH-MT (EPA-EP modified version)	0	18	18
USEPA EP-tox	15	114	129
USEPA TCLP	24	155	179

Table 10. Elements determined in the leachate of components and products [records (components/products)]

Element	Total	Components	Products
Al	66(48)	38(38)	28(9)
As	367(228)	111(32)	256(196)
B	62(31)	18(6)	44(25)
Ba	37(11)	11(6)	26(5)
Ca	211(49)	59(17)	152(32)
Cd	446(164)	151(33)	295(131)
Co	135(44)	60(18)	75(26)
Cr	452(201)	156(34)	296(167)
Cr VI	149(88)	11(5)	138(83)
Cu	398(238)	81(28)	317(210)
Fe	171(80)	70(22)	101(58)
Hg	167(71)	53(19)	114(52)
K	43(13)	16(4)	27(9)
Mg	115(34)	59(17)	56(17)
Mn	186(64)	101(23)	85(41)
Mo	50(8)	19(4)	31(4)
Na	45(11)	16(4)	29(7)
Ni	266(92)	130(28)	136(64)
Pb	594(163)	142(35)	452(128)
Si	72(20)	33(12)	39(8)
Ti	51(13)	19(4)	32(9)
V	42(18)	16(4)	26(14)
Zn	425(202)	146(33)	279(169)

The main metals measured in the leachate are Pb, Cu, Zn, Cd, As, Cr, Ca, Ni, Hg, Fe, Mn, and Cr (VI). From these metals, Pb, Cu, Zn, Cd, As, Ni, Hg, and Cr (VI) are included in the list of constituents of potentially hazardous wastes for the OECD hazardous waste classification.

2.3.3. Other variables of the leachate

Some general parameters are evaluated in the leachates as pH, conductivity, organic carbon, etc., and are shown in Table 11. Since different types of leaching tests are performed, it is very important to know the values of metal concentrations in the leachate at a measured pH and redox potential, and some characteristics of the leaching tests, as the liquid/solid ratio, in order to compare the results obtained from these tests.

The number of components and products where these parameters are measured are shown in parentheses.

Table 11. General parameters measured in the leachate of component and products

Parameter	Leachate		
	Total	Component	Product
Electrical Conductivity	127(94)	77(61)	50(33)
pH	1621(340)	568(106)	1053(234)
Total dissolved solids	39(31)	0	39(31)
Total Organic Carbon	66(30)	0	66(30)

3. CONCLUSIONS

In this work, data of cement/waste products have been analyzed, mainly from two main kinds of references: references showing changes of the cement properties due to its mixing with different wastes: mainly with non-hazardous wastes (medium to high dosages of waste); and to a lesser extent with hazardous wastes (very low dosages, as cement interferences). These types of references typically report composition and mechanical properties, but they do not show very often leaching properties.

References related to solidification/stabilization of hazardous wastes (low to medium dosages of cement), where the information is typically related to compositional and leaching properties of the mixes, but less information is provided regarding mechanical properties.

In general terms, few references report leaching and engineering properties together; In solidification/stabilization of wastes, the leaching behaviour of the treated wastes is the aspect most frequently evaluated for regulatory purposes; however, mechanical properties are also relevant for the disposal of treated wastes on landfills where the material must support high loadings, in order that physical control on leaching can be maintained. In addition, the possible reutilization of wastes after mixing with cement as construction materials should also be conditioned by the environmental risk of their leachate at short and long times.

The *formulation* of cement/waste products is the main key for the final properties of products. However, it can be found in the literature certain lack of information about the formulation of the products:

- first of all, there are very different and sometimes complex ways to report the product formulation, making difficult the standardization of data
- there are some products where the composition of all the components in the formulation is not given; for example, when some vendors and patents protect the formulations
- in other products, the composition of some of the components in the formulation is not given (in several cases, the amount of aggregate), or the relative amount among components is given
- water content is not given in the 28 % of the products.

With respect to the properties reported in the database, the poor amount of data for setting time can be surprising, taking into account the greater amount of strength data. In addition, physical and mechanical properties have been performed using different experimental procedures and sometimes they are evaluated at different sample ages; that makes difficult the comparison of data from different sources. In the same manner, there are different experimental leaching procedures (different liquid/solid ratio, type of leachant, particle size, time of leaching, pH); and also, some selected metals are measured in the leachate, mainly according to the type of waste.

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Waste Materials in Construction
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High-performance concrete for sustainable constructions

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The growth of the world's population and the growing demand for new buildings and infrastructure facilities present us with the prospect of a higher cement consumption, specially in the form of more durable concrete structures. However, the environmental impact caused by the increase in the extraction of natural resources and higher CO_2 emissions has given rise to the search for more efficient, environmentally-friendly constructions. To address these needs, high performance concrete has been employed to increase the durability and economic service life of slender structures, to decrease the specific energy consumption and to reduce the environmental impact of these activities. This material plays a dual role, being both more durable and ecoefficient because of its higher resistance to aggressive agents such as chlorides, carbon dioxide, acid rain and other harsh environmental agents. This resistance is produced by the use of one or more mineral additions such as pozzolans or slags, which are usually polluting by-products in the same environment.

This work describes the retrospect on the relationship between energy consumption, environmental impact and economic cost of Portland cement concrete structures and the role of high performance concrete in the production of more efficient and durable constructions. A case study of 12 mix proportions with binary and ternary mixtures of fly ash, rice husk ash and silica fume, with cement substitutions of up to 50% in mass is presented. The mixtures that presented lower cost and energy consumption were those with higher pozzolan content and lower cement consumption. It was found that high performance concrete is an appropriate material for more durable constructions. Therefore, it is more environmentally friendly due to its lower social and economical costs.

1. INTRODUCTION

The development of industrial activity in the second half of the XX century increased the pressure for a more intensive use of natural resources and energy, especially non-renewable fossil fuels. This had harmful consequences to several ecosystems, not only because of the degradation of the environment caused by intensive mining activity, but also because of the dumping of polluting waste materials and industrial by-products. In the last two decades, the action of governmental and non-governmental agencies, as well as the growing realization in society that our planet is unique and must be protected from predatory exploitation, counterbalanced this aggression. To achieve this, human activity must be kept at a sustainable level that is compatible with the possibilities and needs of each region or country.

sustainable constructions is based on the principle of social equity, where the natural resources are seen as belonging to every one and serving every one. For this reason, they should be managed with little impact on the environment (ecology) under the lowest possible cost (economy). Every stage of the construction process must be grounded on the concept of ecoefficiency, that is, goods and services should be obtained at competitive prices and reduced environmental impact in a level that is compatible with the Earth's capacity of sustaining this utilization. This concept balances both ecology and economy to yield more, using less energy and fewer materials, thereby generating less waste and pollution and increasing reuse and recycling.

If we take into consideration that the construction industry accounts for something in the range of 10-15% of the total worldwide consumption of materials, and that Portland cement and derivatives are the most important materials used by mankind, the ecoefficient production of concrete structures is mandatory if the civil construction sector is to address the trends and anxieties of modern society. This can be achieved by producing buildings and infrastructure systems in a self-sustainable process.

This paper presents some considerations about energy consumption, environmental impact and economical cost of constructions produced with Portland cement concrete, as well as the role of high-performance concrete in the production of more efficient and durable structures. The importance of using mineral additions as cementing materials, especially pozzolans, is discussed. Pozzolans have a dual action in the concrete microstructure. On the one hand, they are a polluting byproduct when disposed of without due care. However, they are also an agent that increases concrete resistance to harmful environments. A case study of twelve concrete mix proportions prepared with fly ash, rice husk ash and silica fume is presented, and the mixes are compared for compressive strength and durability properties. It was found that the mixtures with higher pozzolan content presented the lowest economical cost and energy consumption. It follows that high-performance concrete with the addition of pozzolans is the material of choice for the production of durable structures, being not only more environmentally friendly but, also, possessing lower economical and social costs. Therefore, it is the best option for ecoefficient, self-sustainable constructions.

2. CEMENT, CONCRETE AND THE ENVIRONMENT

Cement and concrete in their use as building materials, in addition to their technical (strength) and economical (cost) importance, play an ecological role in the sense that they allow the rational use of natural resources and that they display characteristics not seen in other materials used with a similar purpose. In effect, the main components of cement, limestone and clay, are widely available and their extraction is usually accomplished with little environmental impact if compared with other building materials. The addition of one or more mineral materials to cement, usually by-products or wastes such as fly ash, slag, rice husk ash or silica fume, increases concrete durability and decreases cement consumption.

Table 1 presents the environmental impact of the production of three structural materials: concrete, iron ore and wood, according to Natural Resources Canada [1, 2]. Mining and quarrying operations for concrete materials and iron ore result in an intensive, but not extensive disruption to the land. In other words, the disruption is complete, soil is removed, but the extension of land disrupted is relatively small. The ecological impact associated with the extraction of wood is more extensive because forests provide many functions, such as the absorption of pollution, climate regulation, soil production, carbon recycling, etc.

Table 1
Environmental impact of resource extraction [1, 2]

Materials	Extent	Intensity	Duration	Significance	Impact index
Concrete components	Low to moderate	Moderate to high	Moderate	Low	Aggregates.: 1.00 Limestone: 1.50
Iron ore	Very low to low	High	High	Very low	2.25
Wood	High to very high	Moderate	Variable, complex	Very high (some sites)	Internal: 2.50 Coastal: 3.25

A previous study by Kreijer [3] presents the results when comparing the ecological effects of metals, polymers, glass, masonry and concrete. He selects the latter as the material with the best cost/benefit relationship because it consumes less energy and water for its production and requires less deforestation and desoiling for the extraction of the components. It also displays good strength and durability properties when compared with the other building materials.

In spite of the environmentally friendly profile displayed by cement and concrete, the growing demand for these materials caused by the populational growth will lead to an increased utilization of raw materials and natural resources. The world population will have reached 6 billion by the year 2000 and 11 billion by 2050. This means doubling the current consumption of cement from 2.2 to 4.4 billion tons, water requirement from 1.2 to 2.3 billion m^3 and aggregates consumption from 22 to 43 billion tons [4].

However, every productive process, especially of Portland cement, generates some amount of pollution. The calcination of calcium carbonate in a furnace to produce calcium silicates (C_2S and C_3S) releases CO_2 in the atmosphere. This CO_2 will be added to fossil fuel emissions resulting in approximately 1 ton of this gas for every ton of clinker produced. At the current worldwide production levels of 1.5 billion tons/year, the cement industry is responsible for 5% of the total CO_2 emissions in the atmosphere, aggravating the greenhouse effect in the planet [5].

In line with current ideas of environmental preservation and conservation, the cement and concrete industries are looking into new alternatives to minimize the negative ecological effects of their activity. The burning of alternative fuels using polluting wastes and by-products and the use of more efficient burners and filters are some actions that have already been taken. In addition, concrete industries are already using reduced clinker content cements, i.e., using a wide range of different mineral additions and concrete mixtures with several types of aggregates, such as recycled materials from the demolition of concrete structures. According to the Environmental Council of Concrete Organizations [6], in some American states estimates run at saving of 50% to 60% from the use of recycled aggregate versus fresh aggregate, taking into consideration savings from disposal costs and potential road damage from the transport of fresh or waste material.

Construction industry professionals are designing high performance concrete structures with higher strength and an extended service life because of its higher resistance. However, the best way to increase the technical performance of concrete structures and to raise the overall financial and economical advantages of this product is to add one or more mineral additions to the concrete composition, mainly pozzolans.

3. THE MINERAL ADDITIONS

Since fire was discovered as an energy source, nature has been the victim of the search for more fuel. Mineral coal has twice contributed to this aggression, the first during mining and the second after burning because of the soil deposition of fly ash and bottom ash. It is estimated that from 30% to 50% of the weight of coal return to the mine as ash. The ground granulated blast furnace slag, a by-product of the cast iron industry poses a similar situation, with 30% of the total production deposited in the storage yard as granulated slag. Agricultural residues such as rice husk or rice husk ash are sources of environmental damage because most often they are stored in the open air causing air and water pollution.

The final destination to be given to these by-products or wastes is the main challenge facing modern technology because of their high production levels and compared with their possible use in industrial scale. These residues possess hydraulic activity (slag) and pozzolanic activity (fly ash, rice husk ash, silica fume) because they have a siliceous-aluminous origin, with amorphous compounds, reacting with water or calcium hydroxide, and in this way can be incorporated into Portland cement because of their binding properties. So, the use of these mineral additions replacing part of the cement, in addition to their technical advantages, is a safe and cheap way to remove these pollutants from the soil surface. They are incorporated into the concrete microstructure in a reliable and economical manner, contributing with energy conservation (less cement consumption) and mineral resources conservation (clay, limestone, aggregates), whose extraction is a source of environmental damage.

These trends are a result of the pressure that governmental and non-governmental organizations exert against the dumping of industrial wastes and byproducts to establish stricter and more costly storage requirements with the aim to minimize any potential damage to the environment. The combination of higher storage costs and the clamor of society for environmental preservation, in addition to the increasing price competition of end products, are giving rise to a renewed interest in these waste materials.

Nowadays, approximately 300 million tons/year of fly ash and an equivalent amount of slag are generated. Rice husk production runs at nearly 100 million tons/year, which is equivalent to about 20 million tons of ash. Several recent papers on structural concrete describe the growing substitution of cement by up to 90% of slag by weight [7, 8], up to or more than 50% of fly ash [9 – 12] and up to or more than 25% of rice husk ash [13, 14]. These papers show the great potential of these mineral additions as replacements for an equivalent mass of cement without causing deleterious side effects to concrete durability, as long as the mixtures are adequately proportioned. In spite of some restrictions to the use of higher pozzolan or slag levels in concrete imposed in the past by some standards or international recommendations, these studies confirm that it is perfectly safe and feasible to use them in concrete structures that require good durability and a service life compatible with its design.

As a consequence, the addition of fly ash, ground granulated blast furnace slag or rice husk ash to concrete mixtures is highly recommended, not only for social reasons but also for their economical advantage. They replace Portland cement, a product with high energy and cost requirements, with one or more types of mineral additions with low economical and energetic costs. This trend is in line with the concept of ecoefficiency, where everybody wins: the producer, because he/she sells a product for a lower cost and, of course, also for marketing reasons also; the consumer, because he/she buys an improved material with good resistance, which guarantees the desired service life to the concrete structure; the society, because the environment is not subjected to as much damaged as it would otherwise be.

4. THE DURABILITY OF HIGH-PERFORMANCE CONCRETE

Concrete has been traditionally employed in durable constructions, where a compatible service life according to the needs of the user is expected, implying in no additional repair or maintenance costs. This is true when one wishes to build something permanent to conserve resources and energy and break the construction-demolition-reconstruction cycle caused by natural disasters such as earthquakes, windstorms or hurricanes.

The increasing durability of concrete structures has been the central focus of those constructions that show premature deterioration because of the steel corrosion or other aggressive agents. A practice in widespread use since the 60s was to increase concrete strength by reducing its porosity and, as consequence, durability would also be improved as a result of the increased strength. However, according to Mehta [15], the long term durability of high strength concrete does not qualify it as a high performance concrete because of the large amount of cement used in its preparation, which may lead to shrinkage-induced cracking. In fact, strength is not always a reliable measure of performance because, according to Hooton [16], a stronger concrete can be produced without necessarily having higher impermeability or durability characteristics, since lower water/binder (w/b) ratios do not necessarily result in lower permeability if cement content is high. This condition means that the concrete would need higher amounts of water, have higher initial porosity, and this would make it more prone to cracking.

High performance concrete (HPC), as a consequence of high strength concrete, first appeared in the early 90s thanks to the advent of superplasticizer admixtures and mineral additions that allowed concrete to be produced with low water/binder relationships and with high workability. The main focus of HPC is to obtain the specified strength for the concrete structure through durability, not durability through strength, in this way reversing the main goal of high strength concrete. This is possible because mineral additions modify the microstructure of the paste by altering the concrete pore structure through physical effects, and changing the particle size through pozzolanic reactions. This modifies the paste structure, making its texture finer and the paste more impermeable. Different characteristics can be obtained by varying the type and content of the mineral addition. In Neville's opinion [17] lower w/b ratios in high strength concrete result in a considerable amount of non-hydrated cement, which ends up functioning as a high-cost inert filler, becoming mandatory the use of supplementary cementing materials such as fly ash, ground granulated blast furnace slag or silica fume, alone or in combination (ternary mixtures). These are used because they are cheaper than cement and produce concrete with better durability.

This strategy of producing higher durability concrete using lower cement content and higher mineral addition contents has been studied by some researchers with the aim of expanding the range of options for producing HPC using local materials for the lowest possible cost. A study by Isaia [12] shows that binary and ternary mixtures of fly ash and rice husk ash replacing up to 50% of the cement had the best performance for the parameters that measure durability, mainly those related to rebar corrosion. Certainly, the lower cement content of these mixtures, all other conditions remaining the same, will result in lower costs and reduced energy consumption, without affecting the durability of the material, as it can be seen below.

5. CASE STUDY

Twelve mixtures are analyzed in this study to evaluate the influence of the type and amount of pozzolanic additions on the energy consumption and cost of concrete mixtures for the same strength value and other related durability parameters. A reference mix with 100% Portland cement and 11 mixes with variable content of fly ash, rice husk ash and silica fume, in binary and ternary combinations as replacements for Portland cement from 10 to 50%, by weight, were accomplished. Table 2 shows the mix proportions and the test results for energy consumption and the equivalent cost for each mixture that met the requirements of the case study. The energy consumption of the cementing materials was calculated using the following unitary values: cement = 4.65 MJ/kg; pozzolans (mean) = 0.20 MJ/kg. The equivalent cost of cement (ECC) represents the sum of weighed costs by m^3 of cementing materials, with the following weights: cement = 1.00; fly ash = 0.50; rice husk ash = 0.6; silica fume = 7.00.

For the comparative study of the tests results, a construction with a hypothetical concrete structure meeting all the following specifications was used: a) axial compressive strength at 91 days ≥ 70 MPa; b) water/binder ratio ≤ 0.40; c) chloride penetration (ASTM C 1202) at 91 days ≤ 1000 C; d) water penetration at 91 days ≤ 10.10^{-9} m.s^{-2}; e) ionic Cl^-/OH^- relationship ≤ 1.00; f) carbonation coefficient ≤ 3.0 mm/year^{0,5}.

Table 2
Quantity of materials, test results, energy consumption and cost

	Pozzolan %			Cem. Mater. kg/m^3				w/b	f_{c91} MPa	MJ/ m^3	ECC kg/m^3	Cl^- Coul.	Cl^-/ OH^-	H_2O (*)	k_{ec} (**)
n.°	FA	SF	RA	PC	FA	SF	RA								
1				572				0.32	70.0	2660	572	1660	1.12	9.2	0.5
2		10		405		45		***0.40***	74.6	1892	720	274	0.78	5.4	1.5
3			10	456			51	0.36	***70.0***	2131	487	970	1.00	7.6	1.5
4		20		360		90		***0.40***	84.5	1692	990	169	0.85	3.2	1.9
5			20	405			102	0.36	73.2	1904	466	612	***1.00***	6.9	1.7
6	25			416	139			0.33	***70.0***	1962	486	559	0.77	6.9	1.9
7	15	10		337	68	45		***0.40***	73.0	1590	686	274	0.89	3.8	2.5
8	15		10	392	79		52	0.35	70.0	1849	463	619	***1.00***	6.0	2.3
9			30	315			135	***0.40***	84.0	1492	396	316	0.81	4.4	1.3
10	50			332	332			0.27	81.0	1610	498	301	0.73	1.8	***3.0***
11	30	20		247	148	98		***0.37***	84.6	1198	1007	88	0.68	2.7	***3.0***
12	20		30	225	135		90	***0.40***	72.0	1091	347	242	0.65	3.0	2.5

Note: data in bold and italics determined the choice of mix proportions.
(*) water penetration: x 10^{-9} m.s^{-2} (**) carbonation coefficient: mm/year$^{0.5}$
FA = fly ash; SF = silica fume, RA = rice husk ash; PC = Portland cement
w/b = water/binder ratio; ECC = equivalent cement cost

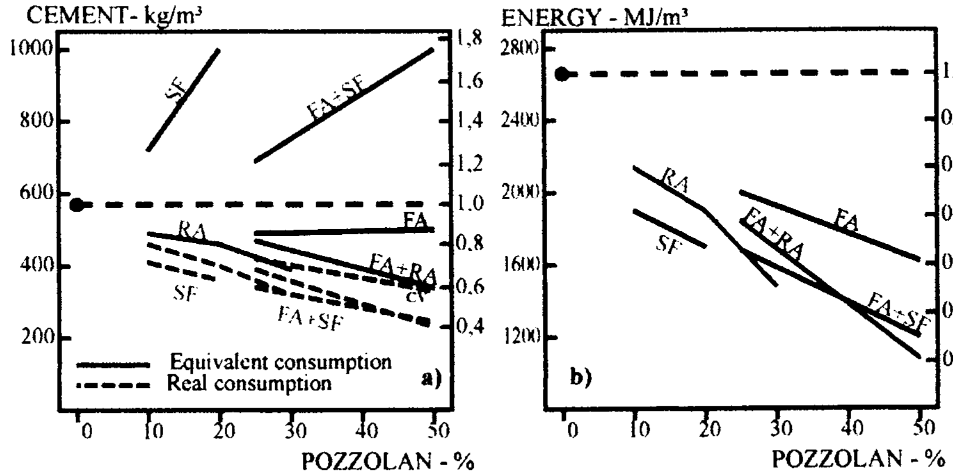

Figure 1. Relations between cement (a) and energy consumption (b) with the pozzolan content in the mxture

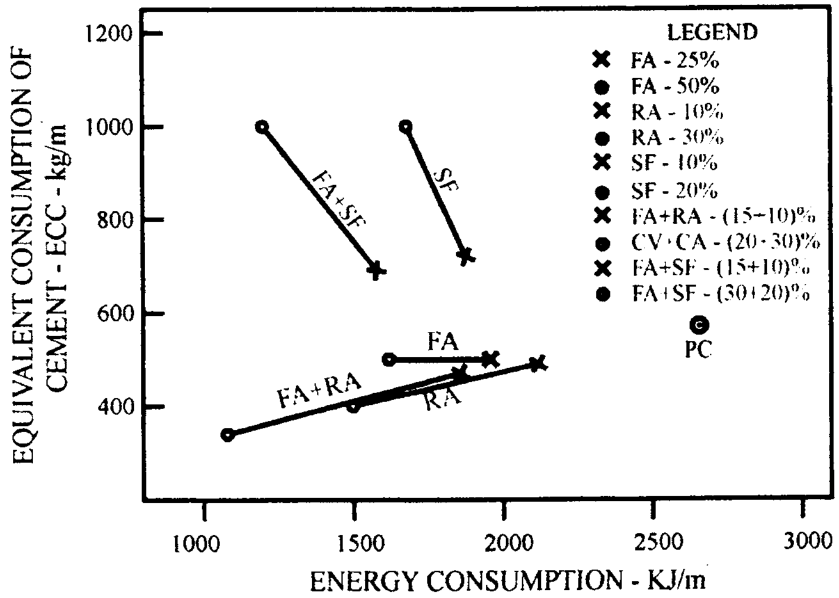

Figure 2. Relations between equivalente content of cement and energy consumption

Figure 1a compares the performance of the mixtures with respect to the quantity of pozzolan and actual or equivalent cement consumption. It can be observed that all mixtures with pozzolans had a lower actual consumption of cement in relation to the reference sample. The fly ash and rice husk ash mixtures had a lower equivalent cost when compared to plain Portland cement, with a reduction of up to 49%, while silica fume samples had a cost up to 76% higher. The best results were found for the mix with fly ash and rice husk ash (50%), with an actual cement consumption of only 225 kg/m^3. Figure 1b presents energy consumption data, showing a decrease as the pozzolan content increased, as expected. The drop ranged from 20% for binary mix with 10% of rice husk ash to up to 59% in a ternary mixture of 20+30% of FA+RA.

Figure 2 relates energy consumption and the equivalent cement cost. It can be seen that a lower pozzolan content in the mixture produces a higher energy consumption and cost for fly ash and rice husk ash mixes. However, the addition of silica fume produces just the opposite effect. In mean relative terms, the mixtures with fly ash and rice husk ash showed a drop between 18% and 49% in energy demand and cost while those with fly ash and silica fume had a cost increase of up to 19%. It can be concluded that from a cost point of view, the use of silica fume does not bring advantages to HPC.

Figure 3 shows the performance of different mixtures with respect to durability. It can be observed that, with the exception of carbonation, the test results for ionic Cl^-/OH^- ratios and water and chloride penetration show an improvement as the energetic content of the mixture decreases (i.e., the cement consumption). The performance for carbonation is the opposite, with the exception of the rice husk ash mixture, since as the cement content decreases(energy amount) so does the alkaline reserve and, as a result, the carbonation rate increases.

Results show that concrete mixtures with a higher contents of pozzolans or with less cement displayed better durability performance. As a consequence, they had a lower energy consumption and less overall cost for the cementing materials used in the mixture.

If we take into consideration that high-performance concrete structures are typically designed with higher compressive strengths so that lower concrete volumes are used in the production of slender slabs, beams and columns per m^2 of structural area, the advantages of using high pozzolanic contents are even higher. In fact, according to Isaia et al. [18], it is possible to have from 12% to 15% reductions in the total volume of concrete in a given structure if high performance concrete is used, when compared with ordinary concrete.

If we take into account the cementing materials only, the global energy reduction of a HPC structure with high pozzolanic content in relation to ordinary concrete, can amount to 60%. In combination with the 12% savings in concrete volume, this represents a reduction of 67% on energy consumption. These figures are valid when 50% of the cement content is replaced with pozzolans such as fly ash or rice husk ash. For mixtures with up to 25% of pozzolan, the energy consumption drops by 33%.

These results attest that concrete, besides being a more environmentally-friendly structural material when employed in HPC structures with high volumes of mineral additions, increases profits because of its ecoefficiency, thus contributing to the production of sustainable constructions.

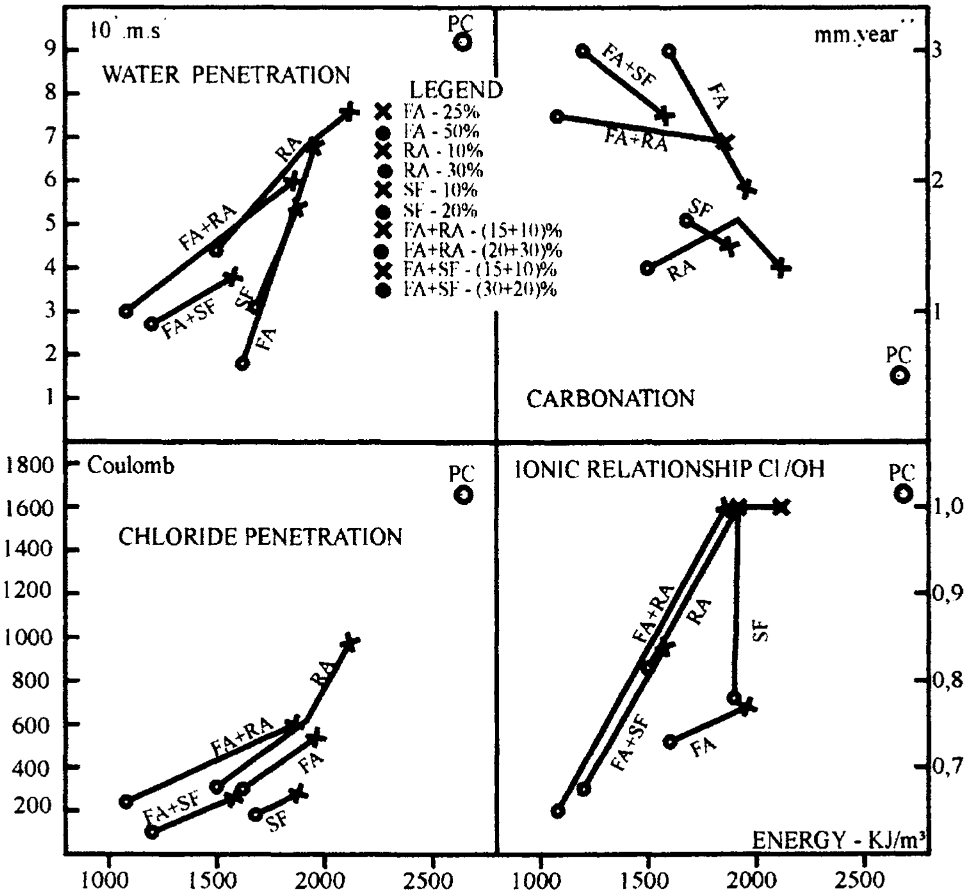

Figure 3. Evolution of durability parameters with energy consumption.

6. CONCLUSIONS

The arguments presented here show that cement and derivatives are the most convenient structural materials available with an optimum cost/benefit relationship, in terms of energy consumption and total cost, because they are made with cheap raw materials and low environmental impact.

The adverse effects that cement and aggregates produce in the environment, especially the former's CO_2-emissions, may be minimized if mineral additions such as pozzolans are used, because they reduce cement consumption, energy and cost. This gain may be increased if high performance concrete is utilized, with the durability criteria predominating over strength.

The case study presented reveals that a reduction of up to 67% of the energy requirements and 80% in the cementing materials cost may be expected when pozzolan additions of up to 50% are used. With 25% of pozzolans added, energy requirements may drop by 33% and cost by 20%. It is possible to produce HPC structures with good durability using only 225 kg/m³ of Portland cement in ternary mixtures with 20% of fly ash with 30% of rice husk ash.

These results show that HPC, with a well-designed mix proportion, produces structures with adequate durability for the desired service life, and it is an efficient material to reduce cost and energy demands of the construction-repair-demolition-recycling-reconstruction cycle, making the construction process self-sustainable and contributing to save economical and natural resources. Above all, it satisfies one of modern society's greatest desires: ecoefficiency.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Significance in the results of total composition and potential leachability of screened MSWI BA from different plants and sampling periods

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The purpose of this study was to determine the environmental properties of sorted and aged bottom ash from municipal solid waste incineration (MSWI BA) and the significant variations in these properties between four plants and four different sampling periods over one year. The non-magnetic 0-50 mm fraction, stored outdoor in 10m^3 boxes for six months, was used. Duplicate samples of the materials were tested for total content and potentially-leachable amounts, with and without oxidising conditions. Inorganic components were analysed. The results were evaluated by means of an analysis of variance and factorial design evaluation. The total content of the samples was dominated by Si, Ca, Fe and Al. Significant differences were found between plants and samples with regard to major component content. The minor components were dominated by Zn, Cu and Pb although significant differences between plants or samples were difficult to identify for Cu and Pb. The potentially-leachable amounts were dominated by Ca for the major components and Cu and Zn for the minor components. Precision in potential leachability was lacking, especially for Cu and Pb. Oxidised conditions increased the leachability of Cr significantly and in some cases also Cu. The overall conclusion from the study was that the results from the determination of total composition or potentially-leachable amounts of minor components need to be evaluated statistically and that comparisons with limit or guideline values need to take the significance of the measured values into account. The experimental errors should be evaluated separately for each element. Moreover, the experimental errors were not a direct function of the average total or leached amounts. Differences in weathering products in the aged material that carried the elements studied also seemed to have an impact on the error in the measurements.

1 INTRODUCTION

Municipal solid waste incineration bottom ash (MSWI BA) is used regularly in various construction applications in many countries, e.g. in road construction (1-4). In the Netherlands, the use of screened bottom ash (non-magnetic, less than 40 mm fraction) was almost 100 % in 1996 (3). Other countries with a high utilisation percentage are Denmark with 90 % (1993) and Germany with 60 % (1993) (2). In Sweden there is no general use of MSWI BA although there have been some minor demonstration projects.

Engineering properties for the use of screened MSWI BA in constructions are generally met (5) and concern is focused on the environmental assessment of the use of the material. Regulations for environmental impact have been developed in the Netherlands (6) and are under development in Denmark (7). Both these regulations put limits on leaching from the materials used in constructions. Several studies have been conducted on the leaching behaviour of MSWI BA under various conditions, including laboratory and field conditions (4, 8-12). Several studies also conclude that geochemical reactions control the leaching behaviour of MSWI BA (10, 13, 14).

MSWI BA has an inherited heterogeneity (4) which is related to the heterogeneity of the incinerated waste. Quality assurance (QA) systems are essential whenever waste materials are used. An important part of a proposed QA system for use in Sweden is that the guideline or limit value for the measurement of the actual parameter should be related to the confidence interval (15). However, the main purpose of most studies of MSWI BA has been to examine the behaviour of the material and few investigations have focused on the effect of heterogeneity on the representativity of test results (16, 17). de Groot and Hoede (16) studied the repeatability and reproducibility of the Dutch availability test (18) on six materials, including MSWI BA. Their results indicate a larger standard deviation for repeatability and reproducibility of potentially-leachable amounts of Cu and Pb in MSWI BA than for the other materials tested.

The results from leaching tests often depend on various parameters, such as pH and redox potential (Eh) (12). Uncontrolled values of these parameters make statistical evaluations of leaching results more complicated. Measurement of the potential leachability according to the availability tests (19, 20) is conducted under controlled pH. In the oxidised availability test (20) Eh is also controlled. Leaching tests with controlled pH and Eh are possible to evaluate using statistical methods, such as analysis of variance (ANOVA) or factorial design evaluation (21). In ANOVA, significant differences between certain groups of values are evaluated. The factorial design evaluation gives the size of the significant difference between groups and the size of the experimental error as determined from non-significant differences.

The purpose of this study was to determine the environmental properties of sorted and aged bottom ash from four municipal waste incineration plants on four different sampling occasions over one year. A second purpose was to determine the significance in the variation of these properties between the plants and sampling occasions. The total content and potential leachability under controlled and uncontrolled Eh were evaluated using ANOVA and factorial design evaluation.

2 MATERIALS AND METHODS

2.1 Materials and sampling

MSWI BA from four different plants was collected during four different two-week periods (September, December, March and June 1996-1997). All four plants incinerate about 200,000 tonnes of municipal solid waste annually. Twenty sub-samples (500 kg) were collected from each plant using a sampling scheme covering a two-week period. The combined sub-samples from each plant were stored in covered containers for two weeks before they were screened to collect the non-magnetic, 0-50 mm fraction. Screening and intermediate storage were carried out at the same location for all samples. The screened samples were stored outdoors in 10 m^3 wooden boxes for six months before laboratory samples were collected. A grid-based sampling scheme was used for collecting sub-samples for the laboratory sample from each of the boxes on each of the sampling occasions. The laboratory samples were air-dried at 50°C and stored in closed containers until further preparation. The test samples were produced by coning and quartering or by the use of sample splitters.

2.2 Total composition

The inorganic components of the materials were tested for total content and for potentially-leachable amounts at uncontrolled redox potential and under oxidising conditions. The total content was analysed after digestion with lithium metaborate melt according to ASTM D 3682-91 (with $LiBO_2$ instead of LiB_4O_7) for the main components (22), and nitric acid in a Teflon bomb for the minor components and certain trace elements (23). All the elements were analysed by Inductively Coupled Plasma Emission Spectrometry (ICP AES). Inductively Coupled Plasma Mass Spectrometry (ICP MS) was used for further determinations of low concentrations. Uncombusted organic matter was measured separately as loss on ignition (LOI) at 550°C (24).

2.3 Potential leachability

Potentially-leachable amounts at uncontrolled redox potential were measured according to NT ENVIR 003 (19) and potentially-leachable amounts under oxidised conditions were measured according to NT ENVIR 006 (20). These tests are both conducted in two steps as pH-controlled batch tests. In the tests, 8 g of material, with a grain size of less than 125 µm (oversized material is size-reduced), is brought into contact with 800 ml of demineralised water in each step. The pH is held at pH 7 for three hours in the first step and at pH 4 for 18 hours in the second step. In NT ENVIR 006, oxidised conditions are maintained by the addition of hydrogen peroxide. All leachates were pressure-filtered with N_2 over 0.45 µm cellulose nitrate filters for the separation of solids. The leachates were analysed for Al, Ca, Fe, K, Mg, Mn, Na, Si, S, As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb and Zn by ICP AES or ICP MS depending on the concentration. Sulphate and chloride were analysed using ion chromatography.

2.4 Statistical evaluation

Significant differences in results from total composition and potentially-leachable fractions of inorganic components between the plants and sampling occasions were tested using analysis of variance (ANOVA) (21). The effects of different sampling occasions and plants on the results were identified by factorial design evaluation (2^5) based on the parameters: plant, sample occasion and replicate samples (21). Log-linear transformation was applied. Significant effects were selected on three standard deviations ($p<0.0025$) based on normal probability. The identified significant effects were used together with the geometric average to constitute a log-linear model for each substance. This model was used to predict a result (total concentration or leached amount) for each set of combinations of plant, sampling occasion and replicate. Evaluations were made either of all 32 values, or of eight values from each plant separately.

3 RESULTS

3.1 Total composition

The total composition of the samples for each plant are presented in Table 1. The samples were dominated by the content of Si, Al, Ca and Fe. The most frequent minor components included Zn, Cu and Pb. The Cd content was high in material from plant A. The measured total content of Al, Ca, Fe, Si, Cd, Cu, Pb and Zn, and the LOI are given for each sample in Tables 2 and 3.

The differences between plants and sampling occasions were significant ($p<0.01$) for all major constituents (ANOVA). Significant differences were also found for most of the minor components. However, there was no significant difference between plants or samples in the content of Cu and Pb revealed by ANOVA. Factorial design evaluations were made for major components (Al, Ca, Fe and Si), for LOI and for minor components (Cd, Cu, Pb and Zn). The predicted results of total composition for different sampling occasions, plants and replicates based on the models derived from the factorial design evaluation are presented in Tables 5 and 6. In the factorial design evaluations no significant differences were found for Al compared with the results from the ANOVA evaluation. In the tables, the experimental error is also given for each mean value (SD factor). This factor is an instrument to discuss the unexplained differences between the results when the effects of the selected parameters are taken into account (21). The SD factor includes errors from sampling, pre-treatment of samples and analysis.

Table 1
Total composition (mg/kg) presented as an average and standard deviation for the four sampling occasions, each with duplicate samples, from plants A, B, C and D.

Plant	A	B	C	D
	Average ± SD	Average ± SD	Average ± SD	Average ± SD
Al	55600 ± 1800	57100 ± 4300	51700 ± 3000	54200 ± 3700
Ca	89800 ± 6300	92100 ± 6500	92200 ± 3500	94100 ± 5400
Fe	80000 ± 14500	87200 ± 6700	73000 ± 3100	56500 ± 8100
K	11500 ± 1400	10900 ± 1800	10400 ± 1600	10800 ± 2100
Mg	11100 ± 900	13700 ± 700	11600 ± 900	11800 ± 1300
Na	29900 ± 1900	32900 ± 3700	29300 ± 1100	46500 ± 3800
P	5700 ± 1600	4100 ± 200	4000 ± 900	5600 ± 1000
Si	190000 ± 19000	209000 ± 7000	216000 ± 26000	229000 ± 11000
LOI	76800 ± 14900	32200 ± 5100	39300 ± 9300	39800 ± 3400
Ba	6220 ± 2900	6390 ± 2900	3930 ± 3800	1460 ± 170
Cd	18.3 ± 5.6	5.1 ± 2.2	8.7 ± 5.1	8.5 ± 6.8
Co	31.6 ± 4.5	25.4 ± 5.1	24.5 ± 6.7	28.6 ± 18.4
Cr	560 ± 46	633 ± 120	476 ± 69	455 ± 44
Cu	3350 ± 1100	3850 ± 2910	2420 ± 740	2650 ± 830
Mn	1200 ± 140	1020 ± 68	1040 ± 290	753 ± 100
Mo	20.2 ± 7.8	30 ± 12	20.2 ± 11.7	14 ± 8.7
Ni	220 ± 78	231 ± 150	149 ± 24	152 ± 83
Pb	1680 ± 660	1330 ± 120	1500 ± 940	1530 ± 760
Sn	119 ± 49	130 ± 69	105 ± 62	214 ± 74
V	38.1 ± 7.9	46.8 ± 8.7	46.5 ± 12	32.5 ± 4.3
Zn	5100 ± 2300	3920 ± 650	3000 ± 550	2910 ± 920

The factorial design evaluation revealed differences between plants and sampling occasions for the total content of Cu and Pb, but only after separate evaluations were made of each plant. However, no result was obtained for Cu at plants A and B due to split normal probability plots, which implied that the series included odd results. At plant C the evaluation of Cu for the separate plants decreased the experimental error considerably while only a small difference for the experimental error was noted for the evaluation of plant D.

The ratio between the maximum and minimum predicted values was less than a factor of 2 for the evaluated main components (Si, Al, Ca and Fe) and a factor of 2-11 for the evaluated minor components (Cd, Cu, Pb and Zn).

3.2 Potentially-leachable amounts

Potentially-leachable amounts were measured in the availability tests under redox potential dictated by the test material and under forced oxidised conditions by the addition of hydrogen peroxide. The measured potential leachability of Al, Ca, Fe, Cl, Cd, Cu, Pb and Zn in each sample is given in Tables 2 and 3. The corresponding L/S ratio, pH and Eh for each test are presented in Table 4. The bottom ash produced slightly-reduced redox potential in the ordinary availability test. The difference in redox potential between the ordinary and oxidised availability tests is presented in Fig 1.

Potentially-leachable amounts without redox control were dominated by the leaching of Ca. For minor components, Cu and Zn were leached most. The most leachable elements in relation to the total content were Ca, Zn and Cd. The introduction of oxidised conditions did not change the dominating components in the leachate.

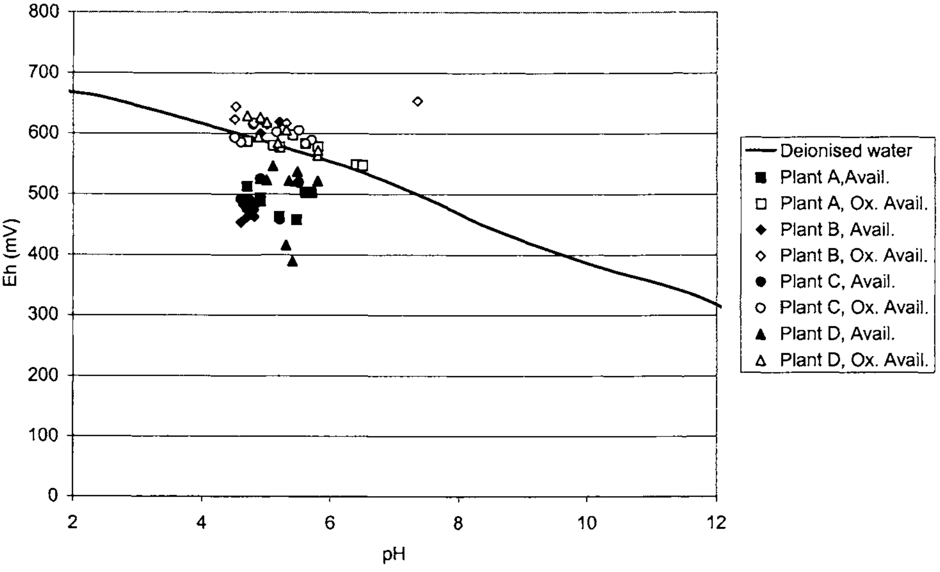

Figure 1 Redox potential as a function of pH in the combined leachates from the availability test and the oxidised availability test.

Table 2 Total content and leached amounts in the availability test (NT ENVIR 003) and the oxidised availability test (NT ENVIR 006) expressed as percent (%).

Plant	Sample	Replicate	Al Total	Al Avail.	Al Ox. avail.	Ca Total	Ca Avail.	Ca Ox. avail.	Fe Total	Fe Avail.	Fe Ox. avail.	Si Total	LOI Total	Cl- Avail.	Cl- Ox. avail.
A	1	a	5.87	0.338	0.229	8.72	3.92	3.59	10.76	0.269	0.0017	17.7	6.5	0.390	0.448
A	1	b	5.77	0.216	0.170	8.37	3.82	3.56	9.65	0.245	0.0011	19.5	7	0.370	0.341
A	2	a	5.35	0.090	0.027	9.64	5.30	4.85	7.97	0.141	0.0004	18.0	9.1	0.539	0.627
A	2	b	5.35	0.063	0.019	9.71	4.58	4.72	7.62	0.064	0.0007	17.7	9.1	0.488	0.505
A	3	a	5.56	0.140	0.233	9.29	4.45	4.98	6.97	0.075	0.0018	17.6	8.9	2.440	1.352
A	3	b	5.50	0.165	0.189	9.51	4.78	4.66	6.66	0.073	0.0014	17.6	9	0.770	1.324
A	4	a	5.56	0.264	0.214	8.29	3.85	3.68	7.20	0.177	0.0012	21.8	5.8	0.474	1.036
A	4	b	5.56	0.215	0.305	8.29	3.85	3.88	7.20	0.122	0.0019	21.8	6	1.187	1.081
B	1	a	6.24	0.234	0.245	8.87	4.05	3.67	8.32	0.210	0.0012	20.9	2.8	0.167	0.198
B	1	b	5.27	0.263	0.255	8.37	4.00	3.46	9.86	0.314	0.0014	20.5	4	0.151	0.186
B	2	a	6.14	0.239	0.305	8.57	3.31	3.23	9.09	0.227	0.0026	22.3	2.69	0.229	0.242
B	2	b	6.30	0.230	0.223	8.71	3.10	2.97	8.11	0.220	0.0014	21.6	2.69	0.224	0.268
B	3	a	5.40	0.242	0.237	9.58	4.08	3.93	8.11	0.181	0.0014	20.6	3.7	1.015	1.071
B	3	b	5.40	0.207	0.208	9.79	4.05	3.88	8.04	0.148	0.0012	20.5	3.7	1.002	1.076
B	4	a	5.50	0.247	0.277	9.93	4.82	4.70	9.09	0.349	0.0019	20.6	3.1	1.018	0.433
B	4	b	5.45	0.251	0.272	9.86	4.98	4.64	9.16	0.359	0.0018	20.5	3.1	1.140	0.400
C	1	a	5.29	0.259	0.268	9.08	4.09	3.96	6.71	0.133	0.0019	22.1	3.8	0.283	0.436
C	1	b	5.61	0.239	0.307	9.01	4.78	4.33	7.41	0.140	0.0025	22.3	3.8	0.225	0.237
C	2	a	4.85	0.178	0.234	9.57	4.92	5.25	7.69	0.263	0.0019	22.6	4.36	0.263	0.384
C	2	b	4.82	0.168	0.106	9.86	4.78	4.91	7.20	0.216	0.0012	21.6	4.36	0.280	0.298
C	3	a	5.40	0.232	0.218	9.43	4.78	4.65	7.41	0.144	0.0014	17.3	4.9	1.670	1.542
C	3	b	5.45	0.154	0.219	9.15	4.27	4.67	7.62	0.115	0.0013	18.0	5	0.669	1.541
C	4	a	4.96	0.175	0.195	8.86	3.89	4.00	7.13	0.144	0.0012	24.4	2.6	1.008	0.451
C	4	b	4.98	0.153	0.172	8.86	3.80	3.78	7.20	0.121	0.0010	24.4	2.6	1.026	0.614
D	1	a	5.82	0.261	0.274	8.65	3.49	3.26	5.26	0.204	0.0016	24.1	3.9	0.200	0.993
D	1	b	6.14	0.155	0.131	9.15	3.40	3.08	4.93	0.071	0.0005	24.4	4.1	0.188	1.009
D	2	a	5.21	0.136	0.143	9.21	3.34	3.46	6.79	0.196	0.0014	22.9	3.47	0.277	0.441
D	2	b	5.45	0.169	0.162	8.93	3.70	3.54	7.06	0.229	0.0018	23.3	3.47	0.237	0.263
D	3	a	5.19	0.165	0.167	10.01	4.18	4.35	5.14	0.086	0.0019	21.7	4.1	0.667	1.290
D	3	b	5.16	0.068	0.187	10.29	3.40	4.45	5.06	0.062	0.0017	21.2	4.3	0.603	1.248
D	4	a	5.18	0.172	0.205	9.51	4.08	4.09	5.47	0.115	0.0008	23.0	4.2	1.030	0.986
D	4	b	5.19	0.181	0.191	9.51	4.16	4.06	5.50	0.120	0.0006	22.9	4.3	0.988	1.026

Table 3 Total content and leached amounts in the availability test (NT ENVIR 003) and the oxidised availability test (NT ENVIR 006) expressed as mg/kg.

Plant	Sample	Replicate	Cd Total	Cd Avail.	Cd Ox. avail.	Cu Total	Cu Avail.	Cu Ox. avail.	Pb Total	Pb Avail.	Pb Ox. avail.	Zn Total	Zn Avail.	Zn Ox. avail.
A	1	a	24.8	10.07	10.03	4690	346	1184	1520	502	263	9150	4046	4545
A	1	b	19.8	9.94	10.46	1970	498	709	1240	268	345	7770	4145	4040
A	2	a	23.4	15.81	15.92	4610	652	1306	2740	59.8	33.0	5240	2894	2758
A	2	b	25.3	15.59	16.12	4630	695	1183	2740	33.5	26.9	5400	2611	2735
A	3	a	14.2	7.95	8.87	2530	620	1193	1190	34.6	49.2	3210	1547	1838
A	3	b	14.1	8.69	8.28	2640	735	926	1290	37.3	42.9	3400	1742	1698
A	4	a	12.4	4.53	5.14	2860	1270	1562	1350	174	170	3290	1746	1814
A	4	b	12.5	4.44	5.11	2850	1167	1640	1380	149	195	3360	1771	1903
B	1	a	4.08	1.34	1.39	2560	869	1480	1100	837	838	3900	1881	1798
B	1	b	4.68	1.26	1.28	11000	1492	2879	1420	655	712	5280	3184	2982
B	2	a	2.22	0.93	1.03	3500	727	1096	1440	133	154	3240	1248	1277
B	2	b	2.47	0.93	1.21	3020	663	1248	1310	148	160	3250	1154	1219
B	3	a	6.43	1.09	0.65	2440	572	1033	1480	173	157	3840	1606	1619
B	3	b	5.06	1.11	1.25	2420	624	865	1340	181	126	3580	1601	1492
B	4	a	8.01	1.15	1.17	2870	717	1554	1240	82.1	73.4	4200	2452	2537
B	4	b	7.69	1.17	1.10	2990	837	1155	1290	98.1	80.1	4110	2529	2218
C	1	a	5.89	3.12	2.81	1430	401	859	3760	2488	2075	2610	1291	1394
C	1	b	5.63	3.00	2.94	1420	394	670	657	78.2	85.9	2720	1115	1134
C	2	a	4.21	2.39	3.10	2130	599	1159	1160	98.1	101	3280	2078	2216
C	2	b	4.63	2.60	2.81	2230	531	990	1230	88.8	83.2	3620	1984	2015
C	3	a	16.8	8.63	9.69	3290	1439	1580	1400	50.5	50.9	3600	2056	2027
C	3	b	16.7	7.31	9.73	3200	800	1523	1400	38.3	46.7	3460	1605	1927
C	4	a	8.08	2.08	2.16	2890	1070	1396	1220	233	232	2360	1027	1031
C	4	b	7.69	2.11	2.10	2780	1005	1319	1190	222	216	2330	991	972
D	1	a	4.36	56.1	154	1910	7540	9810	788	222	251	2690	2284	2216
D	1	b	3.52	2.48	2.19	2620	1250	2073	782	66.5	90.1	2340	1647	1527
D	2	a	4.27	1.76	2.05	3240	1167	2086	2270	593	560	2950	1458	1509
D	2	b	3.82	1.48	1.80	3850	899	2217	2460	534	632	2810	1451	1548
D	3	a	7.52	3.19	2.93	2730	687	974	2350	444	405	4330	3010	2833
D	3	b	6.01	1.89	2.50	3450	320	1247	1770	74.4	196	4210	1457	2533
D	4	a	20.6	3.50	3.86	1710	657	967	941	38.1	39.8	2040	917	994
D	4	b	17.7	3.31	3.92	1680	657	953	885	39.3	38.5	1890	929	982

Table 4 pH, Eh and leachate to solid ratio (L/S) in the availability test (NT ENVIR 003) and the oxidised availability test (NT ENVIR 006).

Plant	Sample	Replicate	L/S Avail.	pH Avail.	Eh Avail.	L/S Ox. avail.	pH Ox. avail.	Eh Ox. avail.
A	1	a	202.3	4.7	513	208.5	5.2	577
A	1	b	204.2	4.9	494	210.4	5.6	584
A	2	a	209.7	5.2	463	208.9	6.4	549
A	2	b	200.8	5.5	458	207.2	6.5	547
A	3	a	203.3	5.7	503	211.2	5.4	598
A	3	b	202.5	5.6	503	210.1	5.8	578
A	4	a	206.1	4.7	479	211.4	5.1	580
A	4	b	204.7	4.9	488	211.9	4.7	587
B	1	a	203.6	4.8	463	205.9	4.8	617
B	1	b	204.1	4.7	473	207.1	5.0	614
B	2	a	204.2	4.7	463	203.3	7.4	653
B	2	b	203.9	4.6	481	206.3	4.5	644
B	3	a	203.0	4.9	599	210.0	4.9	622
B	3	b	204.5	5.2	618	211.0	5.3	616
B	4	a	207.8	4.6	454	196.7	4.5	623
B	4	b	207.3	4.6	453	199.8	4.5	623
C	1	a	202.3	4.6	491	209.6	4.6	585
C	1	b	204.2	4.7	490	210.0	4.5	593
C	2	a	205.8	4.7	481	205.2	4.8	615
C	2	b	206.0	4.7	490	205.4	5.2	602
C	3	a	203.6	4.9	525	211.2	5.7	589
C	3	b	202.6	5.5	519	211.1	5.6	583
C	4	a	205.8	4.8	476	196.3	4.8	617
C	4	b	205.2	5.2	458	198.0	5.5	605
D	1	a	203.9	4.9	525	209.1	4.7	629
D	1	b	204.6	5.0	523	208.1	5.3	605
D	2	a	225.4	5.5	537	209.8	4.9	594
D	2	b	204.4	5.4	522	207.2	5.2	584
D	3	a	202.0	5.1	546	208.0	5.0	618
D	3	b	201.0	5.8	522	208.0	4.9	626
D	4	a	206.0	5.4	389	209.7	5.8	564
D	4	b	205.9	5.3	416	209.4	5.8	572

Evaluation using ANOVA revealed that no significance in differences ($p<0.01$) between plants and sampling occasions was found for Cd, Cu, Pb and SO_4 in the availability test. In the oxidised availability test, Fe was added to this group and SO_4 was removed. An evaluation of the influence of oxidised conditions was also made using ANOVA. The leaching of Cr significantly increased and the leaching of Fe decreased under oxidised conditions in all the samples. In samples from plants B and D, leaching of Cl increased significantly under oxidised conditions. The same applied to leaching of Cu in samples from plants A and C. In addition, leaching of Na, Mn, Ni, Ca and Mg was significantly influenced by oxidation in samples from plant B.

The derived prediction models for the potentially-leachable amounts under uncontrolled and controlled oxidised conditions for the major components Al, Ca, Fe, and Cl, and for the minor components Cd, Cu, Pb and Zn are presented in Tables 5 and 6. The models were based on significant differences ($p<0.0025$) between plants and sampling occasions. The variation in predicted values was less than a factor of 4 for the modelled main components and less than a factor of 8 for the modelled minor components.

Some very different values were observed in the results from sample 1 in plant D (see Table 3). These values were not omitted before the statistical evaluations were made and were included in the prediction models as strongly diverging results may occur. A correction of these values (using the same value as for the other replicate of the sample) in the ANOVA and the factorial design evaluations, revealed differences between plants and sampling occasions for Cd whereas the lack of significant differences remained for Cu. The experimental error evaluated from the factorial design evaluation, expressed as an SD factor, cf. Table 6, decreased for both substances to around 1.05 when the corrected values were used.

4 DISCUSSION

The amount of data in this study has made it possible, but also necessary, to use statistical tools for the evaluation of the measured data. Significant differences in total content and potential leachability for specific plants and sampling occasions were thus revealed. The evaluation focused on the four most prevalent major components, Si, Al, Ca, Fe and Cl, on LOI, and on the interesting minor components Cd, Cu, Pb and Zn.

The total content of the sampled materials were all comparable with the interval for the total content of MSWI BA presented in Chandler et al. (4) except for the fact that the content of Ba is larger in this study. The concentrations of Ba, Co, Cr and Pb in the material from plant A were clearly higher compared with an earlier study of sorted MSWI BA from plant A, where the fraction 2-35 mm was used (12). This difference may relate to the different contents of fine particles in the screened samples.

The potential leachabilities of Ca, Cl, Cu and Pb in the present study were larger compared with results presented in de Groot and Hoede (16). However, this may relate to the difference in the time of the second leaching step between NEN 7341 (3 hours) and NT ENVIR 003 (18 hours). The differences between the tests are discussed further elsewhere (25).

4.1 Variation in the total composition of major components

Some general trends were revealed by the prediction models for the variation in main components between plants and sampling occasions regarding the total content of Si, LOI and Fe. The Si content was lower in samples from plant A, and the Si content increased in

Table 5 Predicted values (%) and SD factor from model evaluated by factorial design.

Plant	Sampling occasion	Al	Al	Al	Ca	Ca	Ca	Fe	Fe	Fe	Si	Cl-	Cl-	LOI
		Total	Avail.	Ox. avail.	Total	Avail.	Ox. avail.	Total	Avail.	Ox. avail.	Total	Avail.	Ox. avail.	Total
A	Sept.	5.63	0.221	0.184	8.58	4.29	3.73	9.80	0.154	0.0013	19.3	0.264	0.49	6.83
A	Dec.	5.63	0.154	0.184	9.68	4.96	5.09	7.61	0.154	0.0013	18.9	0.264	0.49	9.33
A	March	5.63	0.154	0.184	9.39	4.40	4.98	7.39	0.154	0.0013	16.7	0.968	1.24	8.87
A	June	5.63	0.221	0.184	8.32	3.80	3.65	7.07	0.154	0.0013	21.8	0.968	1.24	5.74
B	Sept.	5.63	0.221	0.184	8.75	3.90	3.53	9.13	0.154	0.0013	20.7	0.264	0.288	3.46
B	Dec.	5.63	0.154	0.184	8.64	3.37	3.14	8.35	0.154	0.0013	20.8	0.264	0.288	2.63
B	March	5.63	0.154	0.184	9.62	3.80	4.01	8.17	0.154	0.0013	20.4	0.968	0.727	3.68
B	June	5.63	0.221	0.184	9.74	4.40	4.51	9.21	0.154	0.0013	21.1	0.968	0.727	3.09
C	Sept.	5.63	0.221	0.184	9.06	4.29	4.04	7.00	0.154	0.0013	21.5	0.264	0.288	3.75
C	Dec.	5.63	0.154	0.184	9.65	4.96	4.69	7.65	0.154	0.0013	21.0	0.264	0.288	4.35
C	March	5.63	0.154	0.184	9.35	4.40	4.59	7.72	0.154	0.0013	18.6	0.968	0.727	4.88
C	June	5.63	0.221	0.184	8.78	3.80	3.96	6.84	0.154	0.0013	24.3	0.968	0.727	2.68
D	Sept.	5.63	0.221	0.184	8.71	3.90	3.25	5.40	0.154	0.0013	23.1	0.264	0.49	3.96
D	Dec.	5.63	0.154	0.184	9.12	3.37	3.40	6.95	0.154	0.0013	23.2	0.264	0.49	3.55
D	March	5.63	0.154	0.184	10.2	3.80	4.35	5.02	0.154	0.0013	22.7	0.968	1.24	4.22
D	June	5.63	0.221	0.184	9.71	4.40	4.16	5.24	0.154	0.0013	23.5	0.968	1.24	4.17
SD	Factor [1]	1.011	1.061	1.113	1.003	1.014	1.009	1.010	1.091	1.080	1.008	1.069	1.074	1.011

[1] SD is given as a factor of the geometric mean values since a log-linear model is used. The interval for one SD is given by the division of the mean value by the SD factor and multiplication of the mean by the SD factor respectively.

Table 6 Predicted values (mg/kg) and SD factor from model evaluated by factorial design.

Plant	Sampling occasion	Cd	Cd	Cd	Cu	Cu	Cu	Cu	Pb	Pb	Pb	Zn	Zn TT	Zn
		Total	Avail.	Ox. avail.	Total	Total 1)	Avail.	Ox. avail.	Total 1)	Avail.	Ox. avail.	Total	Avail.	Ox. avail.
A	Sept.	20.5	9.2	10.3	2810	2)	554	1030	1370	249	257	8290	2090	1730
A	Dec.	26.2	9.2	10.3	2810		554	1030	2740	82	82	5050	2120	1940
A	March	14.0	9.2	10.3	2810		1110	1740	1240	82	82	3000	2120	1940
A	June	12.6	9.2	10.3	2810		1110	1740	1360	249	257	3420	2090	1730
B	Sept.	4.2	1.2	1.2	2810	2)	1110	1740	1320	82	82	5090	2120	1940
B	Dec.	2.4	1.2	1.2	2810		1110	1740	1320	249	257	3100	2090	1730
B	March	5.4	1.2	1.2	2810		554	1030	1320	249	257	3810	2090	1730
B	June	8.3	1.2	1.2	2810		554	1030	1320	82	82	4330	2120	1940
C	Sept.	6.0	3.2	3.3	2810	1420	554	1030	3190, 558	249	257	2940	1500	1730
C	Dec.	4.2	3.2	3.3	2810	2180	554	1030	1300, 1370	82	82	3340	1480	1940
C	March	16.3	3.2	3.3	2810	3240	1110	1740	1330, 1330	82	82	3810	1480	1940
C	June	8.1	3.2	3.3	2810	2830	1110	1740	1350, 1320	249	257	2320	1500	1730
D	Sept.	3.9	3.4	3.9	2810	1950	1110	1740	846	82	82	2440	1480	1940
D	Dec.	4.0	3.4	3.9	2810	3290	1110	1740	2200	249	257	2770	1500	1730
D	March	6.8	3.4	3.9	2810	3290	554	1030	2200	249	257	3580	1500	1730
D	June	18.8	3.4	3.9	2810	1950	554	1030	846	82	82	2180	1480	1940
SD	Factor 3)	1.018	1.128	1.157	1.072	4)	1.084	1.076	5)	1.181	1.174	1.019	1.056	1.060

1 Evaluation made on each plant separately for 8 values.

2 Split plot was obtained and evaluation could not be done.

3 SD is given as a factor of the geometric mean values since a log-linear model is used. The interval for one SD is given by the division of the mean value by the SD factor and multiplication of the mean by the SD factor respectively.

4 1.008 for plant C, 1.065 for plant D

5 1.028 for plant A, 1.034 for plant B, 1.068 for plant C, 1.044 for plant D.

material from all plants on the last sampling occasion. These differences were probably related to differences in the glass content of the incinerated waste.

The observed differences regarding unburned material (LOI) and the Fe content may relate to the incineration conditions, such as temperature, retention time and CO. However, these parameters were not recorded in this study. The LOI was almost doubled at plant A on the second and third sampling occasions compared with the results from the other plants, which was most likely a function of the incineration conditions. The Fe content was generally higher in samples from plant B and lower in samples from plant D even though magnetic material was separated from the samples using the same screening equipment.

Iron is predominantly introduced into the incineration plant by the metallic fraction (4). In the MSWI BA, Fe is found in the metallic fraction or in different oxides in the material (4, 10). Differences in Fe content between plants could indicate differences in conditions for the formation of iron oxides in the incineration process or differences in the inclusion of metallic iron in fine particles in the ash. These findings stress the need to link the characterisation of MSWI BA to the incineration conditions.

4.2 Variation in the total composition of minor components

Variations between plants and sampling occasions were easily identified for the total content of Zn and Cd. However, there were difficulties in finding differences in the content of Cu and Pb even though the concentrations were considerably higher than the Cd content. Differences for Cu and Pb were found using the factorial design evaluation, but only after separate evaluations were made for each plant.

The precision of the mean values in the prediction models for Zn and Cd were comparable even though the content of Zn was three magnitudes greater than the content of Cd. The difference in behaviour between Zn and Cd on the one hand and Cu and Pb on the other was clearly not a function of the detection limit for the analysis but was related more to differences in the distribution of these elements in the material.

Stegemann and Schneider (26) found Zn and Cu predominantly in particles less than 2 mm. This effect was more pronounced for Zn than for Cu. If there had been a variation in the fines content of the sub-samples from the boxes this would have caused a heterogeneous distribution of both Cu and Zn. Since the lack of precision was linked to Cu and not to Zn in the present study the lack of precision for Cu could not be related to a presumed variation in the particle distribution between sub-samples. The pattern for the seasonal differences in Pb content was not similar at the four plants and at plant C the differences were even significant between the replicate samples. Eighmy et al (10) identified several minerals that contain Cu and Pb in MSWI BA as well as Cu-alloys. The mineralogy and distribution of Cu and Pb, however, need to be linked to the heterogeneity in samples from MSWI BA.

4.3 Variation in potential leachability of major components

There were major differences in the leaching behaviour of the main components studied. The potential leachability of Ca seemed largely to follow the total content, whereas the leachability of Al, Fe and Cl was less predictable (see Table 5).

A large percentage of Ca is present as $CaCO_3$, $CaSO_4$, $CaCl_2$, CaO and Ca-silicates in aged MSWI BA (27). This may explain the high leachability of Ca since the four first mentioned minerals are easily soluble in the availability test.

The experimental error of the mean values was larger in the prediction models for the potential leachability of Al, Fe and Cl compared with the experimental error for the mean values in the models for Ca. Only some seasonal differences could be distinguished from the error for Al and Cl and no differences could be distinguished for Fe. According to Fällman et al. (27) a large portion of Al and Fe in aged MSWI BA is bound in weathering products such as amorphous aluminium silicates. This may have evened out clear differences between the samples since the samples in this study were also aged.

4.4 Leachability of minor components

There was a clear difference in leachability of Cd between plants, and with the correction of the very different value in plant D, differences between sampling occasions were also revealed. In the case of Cu, Pb and Zn, some significant differences were predicted. However, these effects were doubtful in spite of their significance since the predicted values bounced between two levels in varying combinations (see Table 6).

In the study of aged MSWI BA (27) Cu and Zn were mainly found in amorphous aluminium silicates. Similar leachability, as discussed previously for Al and Fe, with the corresponding weak differences between plants and sampling occasions, would therefore also be expected for Cu and Zn. Meima and Comans (28) confirm this for Cu since they found that leaching of Cu and Pb from aged MSWI BA is controlled by surface complexation on the weathering products (hydrous ferric oxides and amorphous aluminium oxides).

Meima and Comans (28) could not explain the leaching of Cd with their model. In Fällman et al. (27) Cd and Pb were mainly found in the carbonate phase of the aged MSWI BA, and $CdCO_3$ was near saturation in the geochemical modelling of the pore water. Carbonates are leachable in the availability test, which may explain the clear difference in leachabilty of Cd between plants and, with corrected values for plant D, also between sampling occasions. The conclusion in the present study was that the precision in the test of potential leachability of minor components depends on which of the weathering products in the aged material that contained the element.

The correction of the very different values for Cd in one sample from plant D revealed differences between plants and sampling occasions in the ANOVA and the factorial design evaluations. These differences were not seen in the ANOVA evaluation on uncorrected values. However, differences in uncorrected values between plants were revealed by the factorial design evaluation. One conclusion was that it seemed as if the ANOVA evaluation was a less robust instrument than the factorial design evaluation when very different results may be included in the series.

4.5 Experimental error

The experimental error in the study expressed as the SD factor for the mean value in the prediction models is plotted as a function of average amounts in Figure 2. The plot clearly reveals that the errors were not directly dependent on the average amount. The errors in the measurement of the total content of Cu and Pb were larger than the error for the other substances even though the average total contents of Cu and Pb were far from the detection limits for the analytical method. In addition, the error for potential leachability was larger than the error for the measurement of the total content, especially for the potential leachability of Pb. This corresponds to the results from de Groot and Hoede (16), where the largest standard deviations for repeatability in the availability test were found for Pb.

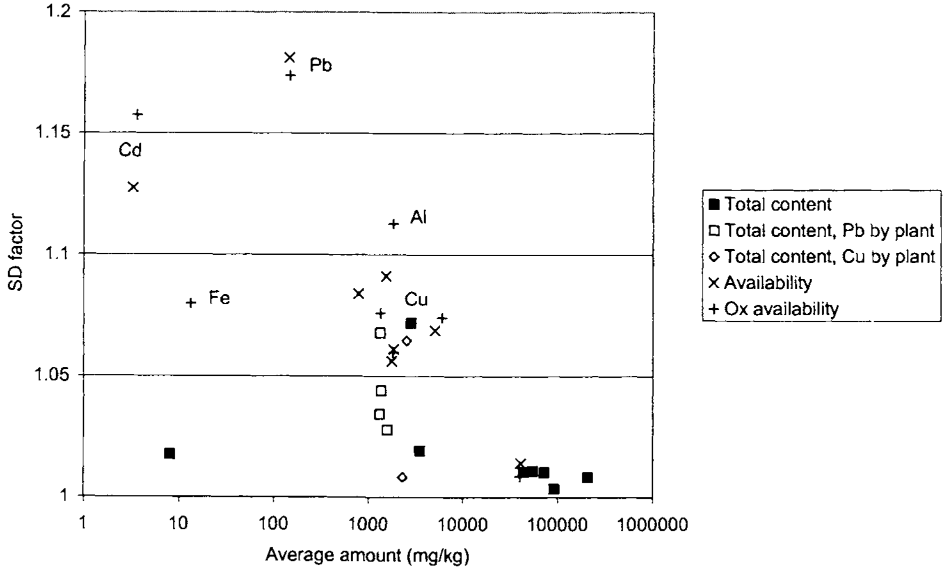

Figure 2 The experimental error in the study expressed as the SD factor for the mean value in the prediction models as a function of average amounts.

4.6 Influence of redox potential in the potential leachability

The materials produced a reduced leaching environment in the availability test without the control of redox potential. The comparison with the oxidised availability test clearly showed different redox conditions in the two test procedures and also significant differences in the leached amounts of certain substances. It is relevant to test MSWI BA under oxidised conditions since all the materials tested showed slightly-reduced redox potential in the availability test (Figure 1) and utilisation will expose the material to oxidised conditions. It is also relevant to compare results from oxidised and non-oxidised conditions.

5 CONCLUSIONS

The overall conclusion from the study was that the results from the determination of total composition or potentially-leachable amounts of minor and trace elements needed to be evaluated statistically. The experimental errors should be evaluated separately for each element and, moreover, they were not directly related to the average total or leached amounts. The difference in weathering products in the aged material that carried the elements studied also seemed to have an impact on the error in the measurements. It became clear that there will be a need to consider the inherited variation in the results for specific elements in different tests when guideline or limit values for the utilisation of MSWI BA are to be decided. The generation of test results for comparison with different limit values will therefore need a number of independent measurements to produce a mean value and a standard deviation.

6 ACKNOWLEDGEMENT

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Effect of mineral admixtures on some properties of sand-lime bricks

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The effect of mineral admixtures used in the production of autoclaved sand-lime brick was investigated. The waste materials and by-products of pozzolanic properties- fly ashes, microsilica, were added to the mixture composed of quartz sand and burnt lime. The hydraulic admixture-granulated blast furnace slag and activators (gypsum, etc) were also taken into account.The phase composition and microstructure of materials were characterised using XRD, SEM + EDS and mercury porosimetry. The standard mechanical properties of sand-lime brick were also determined, including absorbability: leaching was not, however, investigated.

1. INTRODUCTION

Quartz sand and burnt lime are the traditional starting materials in sand-lime brick production [1,2]. These materials, mixed and formed, are subsequently autoclaved, to transform lime and silica into hydrated calcium silicates of different structure [3-5]. The amorphous phase calcium silicate hydrate (C-S-H), being the first product, is the precursor of tobermorite and other phases synthesised in hydrothermal conditions [6]. In practice, same impurities in the raw mixture can give the other products; in the presence of aluminium ions the stabilisation of tobermorite occurs [7] or even the formation of hydrogarnets takes place [8]. The latter phase affects significantly the strength of final product.

The mechanical properties of autoclaved products are strongly related to the total amount of C-S-H and tobermorite [9]. Hence the materials should be processed with aim to produce the highest content of these phases. Such an effect can be achieved by incorporation of same admixtures.

The phase composition and microstructure of autoclaved products is thus modified by use of fly ash, microsilica and ground granulated blast furnace slag. These admixtures bring about the formation of additional C-S-H and subsequently tobermorite, as a result of pozzolanic reaction. Simultaneously the capillary porosity of materials is reduced and consequently their strength and quality is increased [10].

The waste materials and by-products of pozzolanic character, e.g. fly ashes, slags, silica fume can be used in silicate building materials technology. Also very promising is the potential incorporation of a "new generation" of wastes (i.e. gypsum, etc) from the desulphurization operations in the same fluidised bed combustion (FBC) installations.

These wastes exhibit high pozzolanic activity resulting from the presence of decomposed clayey mineral - metakaolinite. Same amount of $CaSO_4$ and $CaCO_3$ can promote the formation of hydroellastadite [11] or scawtite [12,13] in hydrothermal conditions. The microstructure of materials is thus modified.

Some of the waste materials from the groups mentioned above show their pozzolanic activity, under the presence of alkalis or sulphates [14,10]. Thus the determination of the effect of some ions on the formation and properties of hydration products during autoclaving is of special importance from both practical and scientific point of view.

2. CHARACTERISTICS OF STARTING MATERIALS

The two main commercial components were taken in the production of sand-lime brick: quartz sand and burnt lime, meeting all the standard requirements. The following mineral admixtures of pozzolanic and/or hydraulic properties were also used:

- fly ash from black coal combustion (Pl - S)
- fly ash from fluidized bed combustion (Pl - Ż)
- ground granulated blast furnace slag (Pl - HTS)
- microsilica (Pl - A)

The natural gypsum, anhydrite, 0.5 M NaOH solution and water glass of silica modulus 2.5 were used as activators. The chemical composition and some properties of admixtures are given in Table 1 and 2.

Table 1
Chemical composition of mineral admixtures

Component	Pl - S	Pl - Ż	Pl - HTS	Pl - A
	Percentage, in weight %			
SiO_2	51.50	55.12	39.38	93.84
Al_2O_3	25.90	17.36	6.13	0.89
Fe_2O_3	8.60	4.68	0.35	0.45
MgO	2.10	0.37	8.25	0.46
CaO	2.20	12.69	43.76	1.49
SO_3	3.17	5.20	n.a.	0.17
Mn_2O_3	0.13	0.90	0,47	n.a.
K_2O	2.55	1.93	0.95	0.96
Na_2O	1.75	0.92	0.51	0.47
CaO_{free}	n.a.	4.82	n.a.	n.a.
Unsoluble	2.1	0.83	2.13	2.7
L.O.I.	1.45	0.79	0.57	1.37

Table 2
Selected physical properties of mineral admixtures

Parameter	Pl - S	Pl - Ż	Pl - HTS	Pl - A
Blaine specific surface, m^2/g	370	310	425	390
Specific density, g/cm^3	2.21	2.66	2.93	2.25
ASTM pozzolanic activity, wt. %				
SiO_2 active	9.24	12.84	-	19.13
Al_2O_3 active	3.40	4.62	-	0.73

3. SAMPLE PREPARATION

The samples were produced as series 1 to 3 and 4 to 5. In the first series (1,2,3) the total content of sand and admixture was 92.0%, with different proportions of these components and constant percentage of lime 8.0%. In the second series (4,5) the lime content was lowered up to 6.0% and constant silica to lime ratio, the admixture percentage was higher.

In all cases the components were preliminary homogenised without water and subsequently wetted with 8 - 10% H_2O to produce the material for further processing. After heating at 60°C for 4 hours in sealed container to slake the lime component, the 30 x 30 mm or 50 x 50 mm cylinders were shaped with help of hydraulic press with steel matrix. This operation was completed in three steps: two deaeration steps at 5 and 10 MPa respectively and final pressing at 20 MPa. The cylinders thus formed were subsequently autoclaved in industrial installation for cellular concrete production. The parameters of hydrothermal treatment were as follows:

- saturated steam pressure - 1.3 MPa
- temperature - 190°C
- time of autoclaving - 16 hours

After this the samples were subjected to the standard tests and studies of phase composition and microstructure to determine the relationship between the type of admixtures and activation on the quality of autoclaved materials.

4. PHYSICAL PROPERTIES OF AUTOCLAVED MATERIALS

The following properties were measured:

- compressive strength R_c, MPa
- absorbability N_m, %
- bulk density C_0, kg/dm^3
- freeze-thaw damage.

The results for particular series are given in tables 3 to 6.

Table 3
Physical properties of series No 1 samples

Sample	Admixture		Property	
No	Type	Content	R_c, MPa	C_0, kg/dm^3
1 - 0	-	-	28.7	1.8
1 - I	Pl - S	30.0 %	37.6	1.9
1 - II	Pl - HTS	10.0 %	39.0	1.8
1 - III	Pl - A	10.0 %	11.4	1.6
1 - IV	Pl - Ż	30.0 %	16.4	1.7

Table 4
Physical properties of series No 2 samples

Sample No	Admixture		Type of activator							
			0.5 M NaOH		Gypsum		Anhydrite		Water glass	
	Type	Content	Parameter							
			R_c	C_0	R_c	C_0	R_c	C_0	R_c	C_0
2 - 0	-	-	10.5	1.8	19.6	1.8	16.3	1.8	22.0	1.8
2 - I	Pl - S	30.0	25.5	1.8	44.9	1.8	42.1	1.9	20.6	1.7
2 - II	Pl - HTS	10.0	22.4	1.7	23.2	1.7	13.8	1.8	24.0	1.8
2 - III	Pl - A	10.0	8.2	1.6	10.6	1.7	5.4	1.5	9.1	1.6
2 - IV	Pl - Ż	30.0	17.6	1.7	16.7	1.7	17.4	1.7	14.3	1.7

Table 5
Physical properties of series No 3 and series No 4

Sample	Admixture		Activator		Parameter	
No	Type	Content	Type	Content	R_c	C_0
		Lime content 8.0 % (series No 3 samples)				
3 - I	Pl - S	30.0%	-	-	37.6	1.9
3 - I/A	Pl - S	30.0%	gypsum	0.4%	44.9	1.8
3 - II	Pl - HTS	10.0%	-	-	39.0	1.8
3 - II/A	Pl - HTS	10.0%	water glass	10.0%	24.0	1.8
		Lime content 6.0% (series No 4 samples)				
4 -I	Pl - S	34.0%	-	-	43.0	2.0
4 - I/A	Pl - S	34.0%	gypsum	0.4%	46.1	2.0
4 - II	Pl - HTS	12.0%	-	-	23.0	1.8
4 - II/A	Pl - HTS	12.0%	water glass	10.0%	19.7	1.8

Table 6
Physical properties of series No 5 samples

Sample	Admixture		Activator		Parameter		
No	Type	Content	Type	Content	R_c	C_0	N_m
			Lime content 6.0%				
M_1	Pl - S	34.0%	-	-	34.0	2.0	10.5
M_2	Pl - S	34.0%	gypsum	0.4%	42.4	2.0	8.8
M_3	Pl - HTS	12.0%	-	-	20.1	1.8	14.8
M_4	Pl - HTS	12.0%	water glass	10.0%	18.1	1.8	16.5

It is evident that pozzolanic or hydraulic admixtures bring about a significant compressive strength increase. The effects of fly ash Pl - S and granulated blast furnace slag Pl - HTS are most pronounced in all series of samples. The further activation of each fly ash Pl - S based sample by use of the same (0.4%) gypsum gives further strength improvement.

5. PHASE COMPOSITION AND MICROSTRUCTURE OF SAMPLES

The samples from series No 5 were subjected to the examinations of phase composition and microstructure by means of XRD, SEM and mercury porosimetry. These samples give the best results of standard tests.

5.1 Phase Composition

The phase composition was determined using Philips PW - 1040 difractometer. The identification of peaks was done basing on JCPDS data. The following samples were examined:

M_0 - produced from quartz sand and lime mixture,
M_1 - produced from basic mixture with fly ash Pl - S admixture,
M_2 - produced from basic mixtures with fly ash Pl - S admixture activated with gypsum,
M_3 - produced from basic sand-lime mixture with granulated slag Pl - HTS admixture
M_4 - produced from basic mixtures with granulated slag Pl - HTS activated with water glass

The XRD patters are plotted in Figs. 1 to 3. The following abbreviations were used to describe the XRD peaks: Q - quartz, CH - calcium hydroxide, CSH - C-S-H phase, T – tobermorite, X - xonotlite, CS - gypsum.

In Fig. 1 the XRD pattern for M_0 sample synthesised from quartz sand and lime, with no admixture or activator, is shown. As one could expect, the peaks from unreacted quartz are

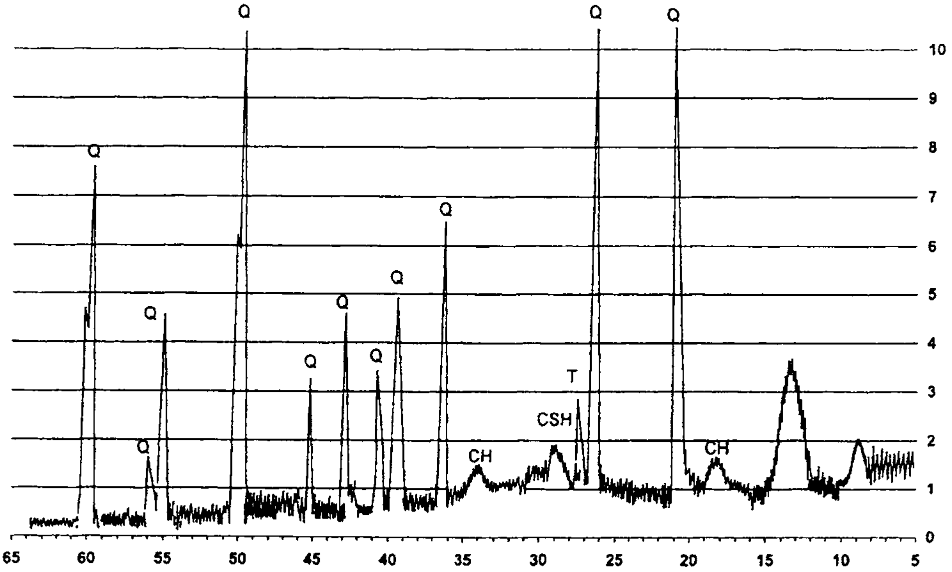

Figure 1. XRD patterns of sample M_0 autoclaved from sand quartz and lime mixture.

present (d = 0.4255, 0.334, 0.2457, 0.2237, 0.2128, 0.1802, 0.1658, 0.1541 nm) but there is no peak from $Ca(OH)_2$. Lime component entreated the reaction products such as C-S-H (d = 0.307, 0.280, 0.240 nm) and tobermorite (d = 1.13, 0.328, 0.228, 0.167 nm).
In Fig. 2 the XRD patterns for sample M_1 synthesised with fly ash Pl - S is plotted. The same phases as in case of sample M_0 are detected: unreacted quartz, C-S-H and tobermorite. The XRD plot for M_2 sample activated with gypsum reveals same peaks attributed to this phase (d = 0.7634, 0.3067, 0.2681 nm).

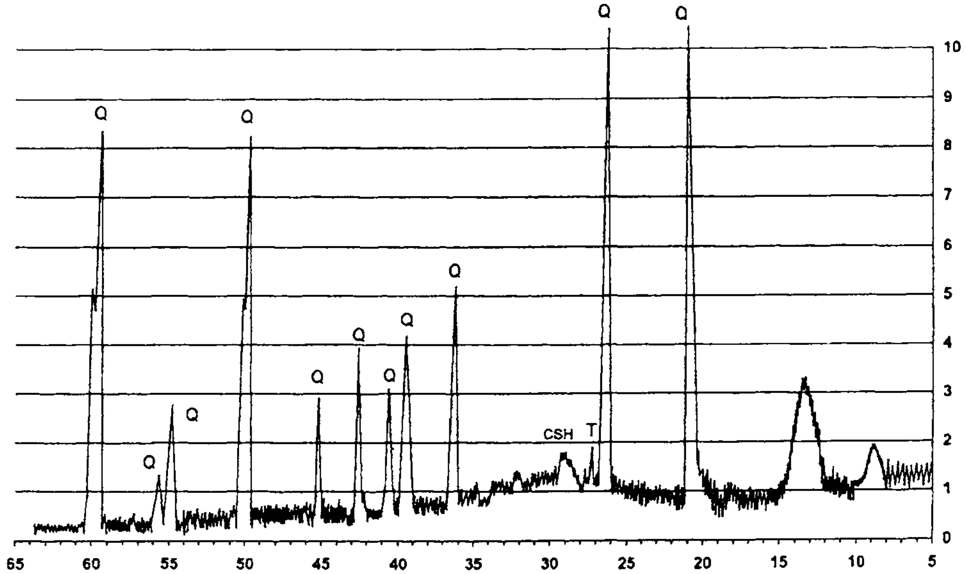

Figure 2. XRD patterns of sample M_1 autoclaved from sand quartz and lime mixture with fly ash (Pl - S) admixture.

In Fig 3. the XRD pattern of M_3 sample synthesised with ground granulated blast furnace slag Pl - HTS, is presented. Apart from the peaks originating from unreacted quartz there are also the peaks of calcium hydroxide (d = 0.4902, 0.2625 nm). This would indicate the possibility of the lime component lowering in the initial batch. Among the reaction products which would be expected, that is C-S-H and tobermorite, some amount of xonotlite is also detected (d = 0.3236, 0.2702 mn). The latter appear usually by further transformation of tobermorite.

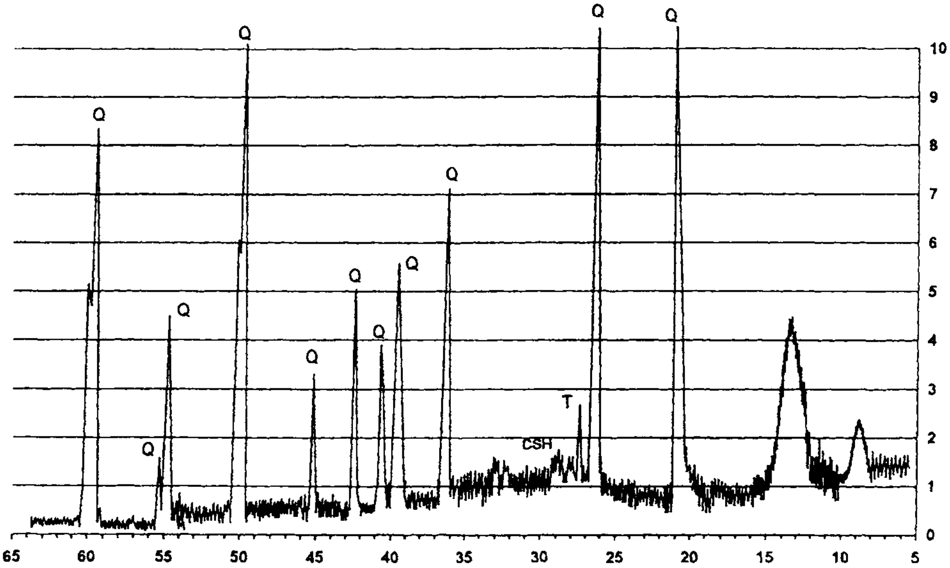

Figure 3. XRD patterns of sample M_3 autoclaved from sand quartz and lime mixture with granulated blast furnace slag (Pl - HTS).

5.2 Microstructure

The microstructure of autoclaved products modified by use of admixtures or not was observed under SEM with help of JEOL JSM-5400 microscope with Oxford Instruments LINK ISIS 300 EDS microanalyser.

The same samples as in case of phase composition studies were taken into account. The results are documented in Figs. 4 to 8. In Fig. 4 the average microstructure of M_0 fractured sample is shown with more or less developed hydration products. The different C-S-H forms are present as well as the lath-like and needle-like elongated tobermorite crystals.

In Fig. 5 the microstructure of autoclaved sample M_2 with fly ash (Pl - S) admixture is shown. There are also nearly amorphous and more shaped products with narrow needle-like tobermorite crystals. At gypsum addition (Fig. 6) the tobermorite occurs in the forms of sharp arrows. The fibrous products grow on the surfaces of fly ash spherical particles - the activity of this admixture is thus documented.

In Fig. 7 the microstructure of M_3 sample is shown. The amorphous, sponge-like porous C-S-H together with plate-like tobermorite crystals are observed. The fibrous C-S-H is dominating product present on the fractured surface of M_4 sample (Fig. 8). One can conclude that this type of C-S-H is synthesised when slag and water glass are added to sand-lime mixture.

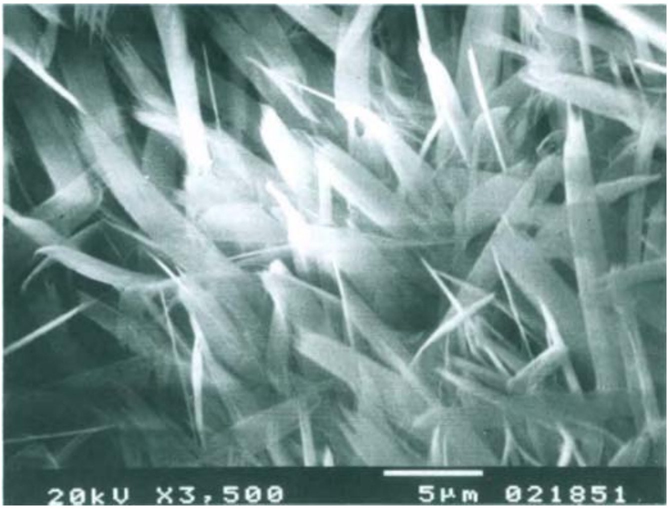

Figure 4. SEM of fracture surfaces of sample M_0 autoclaved from sand quartz and lime mixture.

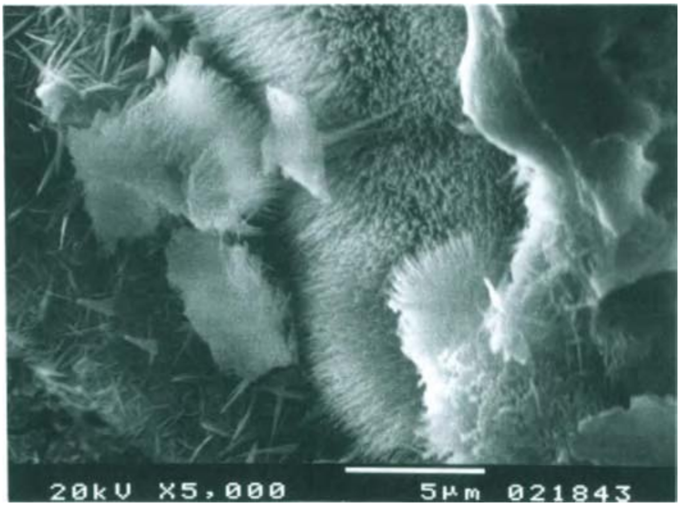

Figure 5. SEM of fracture surfaces of sample M_1 autoclaved from sand quartz and lime mixture with fly ash (Pl - S) admixture.

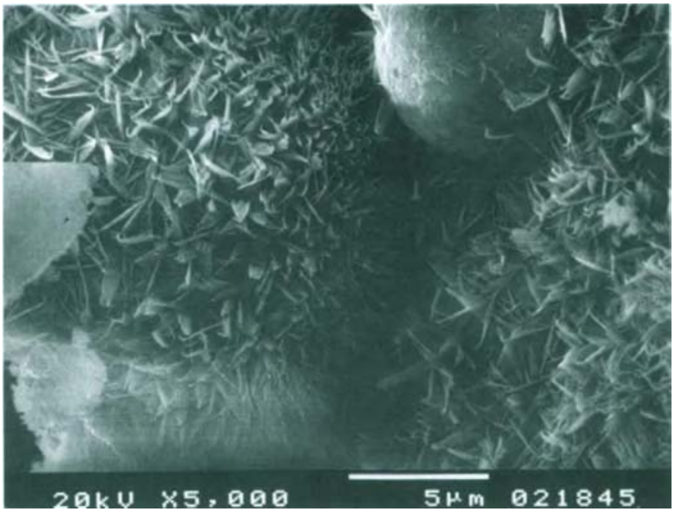

Figure 6. SEM of fracture surfaces of gypsum activated sample M_2 autoclaved from sand quartz and lime mixture with fly ash (Pl - S) admixture.

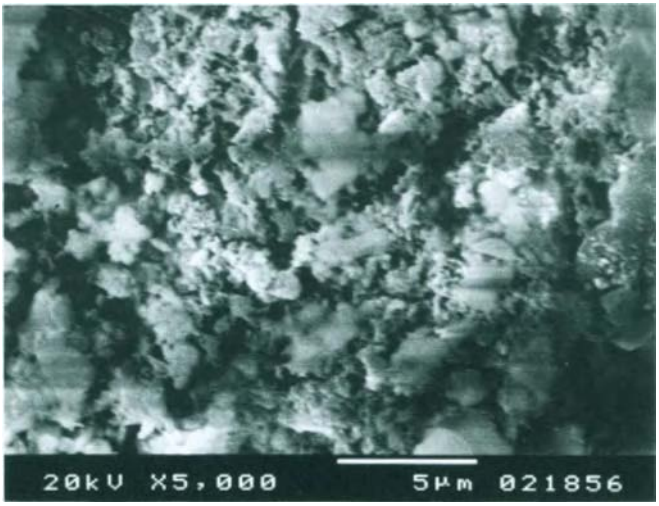

Figure 7. SEM of fracture surfaces of sample M_3 autoclaved from sand quartz and lime mixture with granulated blast furnace slag admixture.

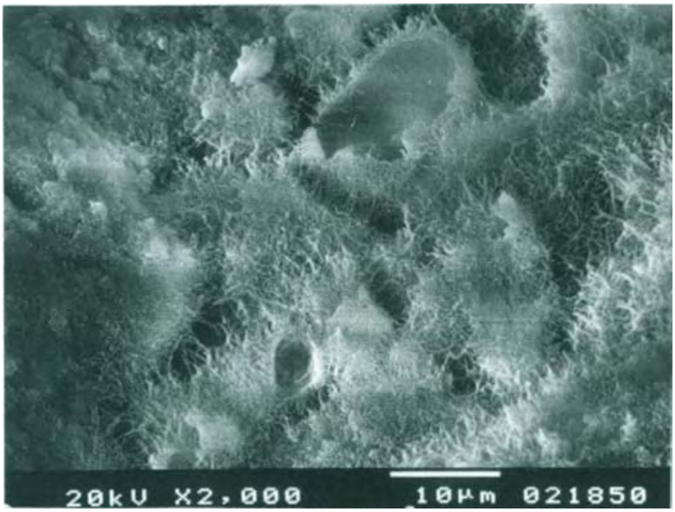

Figure 8. SEM of fracture surfaces of water glass activated sample M_4 autoclaved from sand quartz and lime mixture with granulated blast furnace slag.

5.3 Porosity

The porosity and pore size distribution measurements were carried out using the mercury porosimetry by means of Carlo-Erba PO - 225 porosimeter, in the range above 0,75 nm pore diameter. The results are shown in Fig. 9. The curves for 5 samples are plotted together, to visualise the effect of admixtures. The M_0 sample produced as, ordinary sand-lime material without admixture shows the highest porosity among all the samples. The main fraction consist of capillary pores with 4 ÷ 120 nm radius. The samples M_1 and M_2 produced with fly ash admixture have lower porosity, about half of the value for M_0 in case of M_2. The total porosity is reduced because of the very low content of pores with diameter in the range from 1 000 to 10 000 nm is a dominating one.

The macropores can be the consequence of shaping process in which the empty spaces are filled or not with semi-dry material. The results for M_3 and M_4 samples produced with slag admixture indicate a significant capillary pores content, from the 4 - 20 nm and 50 - 120 nm ranges.

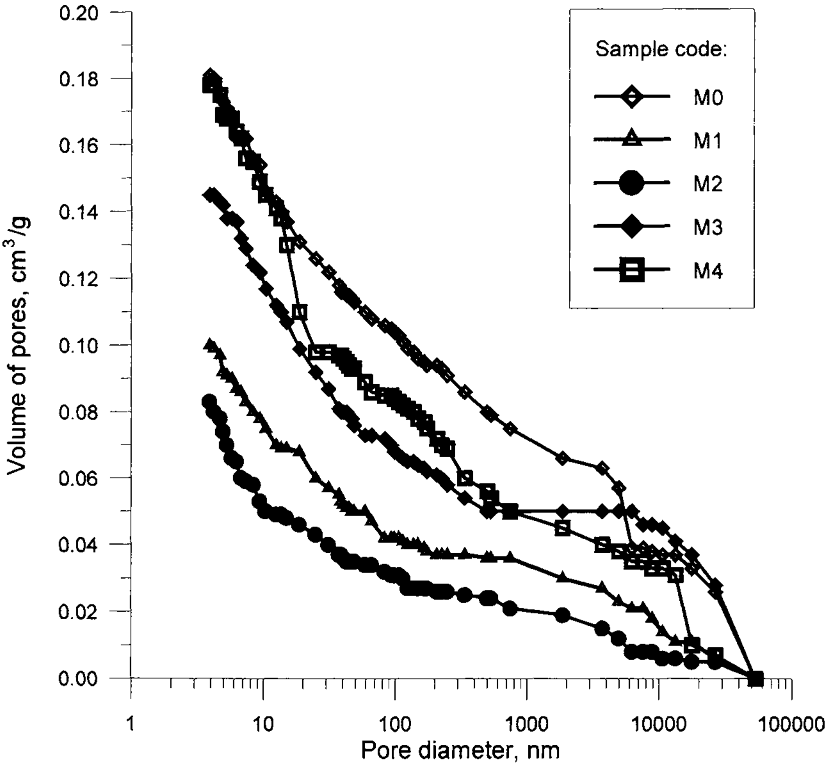

Figure 9. Pore size distribution.

6. SUMMARY

The effect of pozzolanic and/or hydraulic admixtures on the properties of sand-lime brick was investigated. The modification of structure, as a result of pozzolanic reaction between the active components of admixtures and $Ca(OH)_2$ with the formation of C-S-H and other hydrated aluminosilicates, was expected to increase the strength and durability of autoclaved materials. The effectiveness of admixtures is different as it results from numerous experiments. The materials produced with some fly ash (Pl - S) and granulated blast furnace slag (Pl - HTS) show the best strength properties. Activation by use of gypsum and water glass brings about further improvement of standard properties. Thus the burnt lime content could be reduced from 8% to 6% without significant change of properties. At fly ash content of 30% and burnt lime 6% with gypsum activator the sand-lime brick class 15 (the highest) is produced. The admixtures give generally the reduction of total porosity thus improving the strength and durability (see Fig. 9). The samples without admixtures show the highest porosity. The porosity decrease is observed as the fly ash or slag is introduced to the batch and further as an activator is used. There are physical and chemical interactions between the admixtures and initial batch resulting in the reaction in total porosity. Very fine grained admixtures favour the formation of a compact structure on pressing, filling the empty spaces between the grains of the sand-lime batch. As a consequence the biggest pores disappear. The formation of hydration products between the pozzolanic admixture and $Ca(OH)_2$, mainly the C-S-H gel-like structure and low porosity, is the „chemical" aspect of porosity decrease.

ACKNOWLEDGMENT

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Recycling of partially hydrated concrete

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Concrete having a 28 days compressive strength of 28 MPa was crushed at 1, 3 and 28 days to serve as a source for aggregates for a new concrete, simulating the situation exists in pre-cast concrete plants. The properties of the recycled aggregate and of the new concrete made from it were tested.

Significant changes were observed when comparing the properties of the aggregates based on the various size groups of the aggregates, but not when comparing the effect of crushing age. The properties of the concrete made with the recycled aggregates were only slightly affected by the crushing age when the cement matrix of the new concrete was relatively weak, but some effects were seen for a stronger cement matrix.

1. INTRODUCTION

The use of waste from building materials as aggregates for the production of new concrete has became more common in the recent decade. The increasing charge for landfill on the one hand, and deficiency with natural recourses for aggregates on the other hand, encourages the use of waste from construction sites as a source for aggregates. Some successful projects were reported lately, in which waste from the demolition of old structure was recycled into a new one (Collins, 1996, Tavakoli and Soroushian, 1996). RILEM committee 121-DRG (1994) published recommendation for the use of recycled aggregates. They classified the aggregates into three groups: Group I: aggregates that are mainly from masonry rubble; Group II: aggregates that are mainly from concrete rubble; and Group III: mixture of natural aggregates (>80%) together with rubble form the other two groups (with up to 10% of Group I). Group III can be used for the production of all type of concrete and restrictions exist on the other groups. This definition highlights the one of the major difficulties in the recycling demolished waste: the variability of the quality of the recycled aggregates. As long as the aggregates come from a single source, as in the case of highway replacement (Tavakoli and Soroushian, 1996), uniform aggregates source is guaranteed. However, when the aggregates source is a center for recycling aggregates, the rubble arrives from various sources and the properties of the aggregates are not uniform leading to difficulties in using them to produce new concrete (BRE, 1993; Hansen and Narud, 1983).

Apparently, no problem should exist in recycling concrete in pre-cast concrete plants. The various products are routinely made from the same type of concrete and therefore the problem of variability in the properties of the rubble should not exist. However, products are often rejected during the manufacturing process and the concrete of these elements is not properly cured. As a result the properties of the recycled aggregates may vary as well. The effect of partially hydrated concrete on the properties of the aggregates made of it and the resulting properties of new concrete made from these aggregates is reported in this study.

2. EXPERIMENTAL PROGRAM

The experimental program consisted of in two stages: 1) comprehensive study of the properties of concrete made of partially hydrated concrete; 2) study the effect of fines on the properties of the new concrete. This paper presents the results of stage 1 of the study.

Old concrete is made of concrete elements used for standard tests in the process of quality assurance of cement manufacturing. Ordinary Portland Cement (OPC) from the cement plant is produced continuously in almost the same mineralogical composition and the compressive strength is tested routinely by mixing the cement with standard aggregates, in a standard process. Table 1 lists the mix composition for the old concrete.

At ages 1, 3 and 28 days cubes of 100x100x100 mm made from the old concrete were tested for compressive strength. Immediately after the compression tests the cubes were crushed by a mini jaw crusher and dried in an oven at 105°C to cease any further hydration. Good manufacturing in the plant enabled the acceptance of uniform concretes despite being cast in different ages. Table 1 lists the average compressive strength and standard deviation of the old concrete. The new concrete was prepared from 100% of the crushed old concrete with the addition of some natural sand that was needed to maintain good workability. Two types of cements were used for the new concrete, white Portland cement (WPC) and ordinary Portland cement. It was expected that it would be possible to distinguish between the new and old cements by using the white cement. However it appeared lately that the fine aggregate from the crushed concrete that was made mainly of old cement dispersed well in the mix and eliminated the distinction between new and old cement. It should be noted however that the OPC was weaker than the white cement (a compressive strength of 34.6 MPa compare with 42.1 MPa for the white cement, at 28 days). The composition of the new concrete is listed in Table 2.

Table 1: Composition and properties of the old concrete.

Component	Quantity (gr.)
Coarse aggregate (12-25 mm)	5415
Midsize aggregate (2.36-9.5 mm)	1415
Fine aggregate (1.2-0.15 mm)	3120
Portland cement	1800
Water	1080
Compressive strength (MPa) at*:	
1 day	7.4 (0.9)
3 days	14.4 (1.2)
28 days	28.3 (3.1)

*Number in parenthesis - standard deviation

In the followings the term old concrete will be referred to the waste concrete and the new concrete will be referred to the new concrete prepared from the crushed old concrete.

The crushed concrete was sieved over 9.5 and 2.36 mm meshes and were divided to the following size fractions: coarse (larger than 9.5 mm), medium (smaller than 9.5 mm

Table 2: Composition of the new concrete (kg/m^3).

	White cement				Ordinary Portland cement			
	Reference	1 day*	3 days*	28 days*	Reference	1 day*	3 days*	28 days*
Crushed aggregate (9.5-25 mm)	896				907			
Crushed aggregate (2.36-9.5 mm)	448				454			
Crushed sand	212				215			
Natural Sand	421	254	219	238	427	259	217	240
Recycled aggregate		1440	1484	1457		1453	1460	1456
Water	161	160	165	162	163	166	168	163
Cement	294	293	302	296	298	298	300	298

*Age of recycled concrete

and larger that 2.36 mm) and fine (smaller hat 2.36 mm). This was done in order to study the effect of aggregate's size on its properties, and to be able to prepare the new concrete with the same size distribution of the aggregates.

Each size group was tested as follows: size distribution, bulk density, unit weight, water absorption, crushing value (British Standard 812) and cement content.

The new concrete was tested for compressive strength on 100 mm cubes at ages of 7, 28 and 90 days. Four points bending strength, splitting and modulus of elasticity (beams of 70x70x280 mm), rate of capillary absorption of water and total water absorption were tested at 28 days.

3. RESULTS

3.1 Properties of the aggregates made from the crushed concrete

Size distribution curves of the aggregates prepared from the crushed concretes at various ages are presented in Figure 1. The three curves shown in the figure, representing the aggregates prepared from concrete crushed in different ages, show the same size distribution. It appears that as long as the jaw crusher is set to a specific opening there is no significant change in the aggregates grading despite the differences in the concrete strengths they were made from, as seen in Table 1. The 28 days compressive strength of the old concrete was not very high (28.3 MPa at 28 days) and it is possible that the cement matrix between the aggregates was the first to break during the crushing operation. The crack path of normal strength concrete in this range of strengths is known to pass through the cement matrix, and therefore the crushing action led to almost the same size distribution of the aggregates shown in Figure 1.

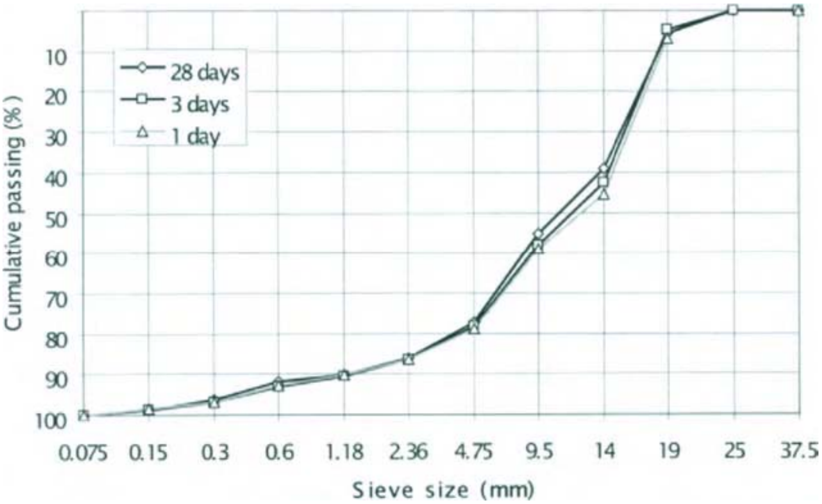

Figure 1: Grading of the recycled aggregates crushed at various ages.

The aggregates were sieved over meshes size 9.5 and 2.36 mm and were divided to three size fractions in order to distinguish between properties that might be related to their size. Table 3 presents the unit weight, bulk density, absorption, crushing value and cement content in the recycled aggregates in the different size groups and crushing ages. Normalized values in which they are compared relative to the value of the coarse fraction crushed at 28 days are presented in Figure 2.

Comparison of the three size groups shows significant changes between the groups. However, the changes with the same size group crushed at different ages, are minor. These changes represent the change in the composition within each size fraction, which seems to be a result of the relative amount of cement paste in the crushed material. As seen in Table 3 the amount of cement (hydrated and not hydrated) significantly increases from approximately 6.5% in the coarse fraction to approximately 25% in the fine fraction. The cement phase is relatively porous and therefore any increase in its relative content leads to a significant increase in the total absorption of the recycled aggregate as their size becomes smaller. The unit weight and bulk density, however, are only slightly changed with the aggregate size. The natural aggregate composes the major phase in the recycled aggregate in all fractions, and the density of the cement phase is only slightly lower than the aggregates. Therefore, the changes in the cement content in the recycled aggregates have only a small effect on their density.

The bulk density of the mid-size aggregates was lower than the one of the fine aggregates (approximately 1240 kg/m^3 compare with 1330 kg/m^3, respectively) despite the lower unit weight of the latter. This phenomenon is probably a result of the better grading of the fine aggregates creating denser packing of the particles in this range.

Table 3: Properties of the recycled aggregates

Crushing age		Unit weight (kg/m^3)	Bulk density (kg/m^3)	Absorp -tion (%)	Crushing value (%)	Cement content (%)
1 day	coarse	2590	1462	3.2	25.4	6.9
	medium	2350	1220	9.7	N/A	15.8
	fine	2230	1324	11.2	N/A	26.6
3 days	coarse	2600	1433	3.4	25.3	6.1
	medium	2380	1234	8.1	N/A	15.2
	fine	2250	1342	11.4	N/A	25.4
28 days	coarse	2550	1433	3.3	24.3	6.8
	medium	2320	1278	8.0	N/A	13.2
	fine	2230	1321	12.7	N/A	24.5

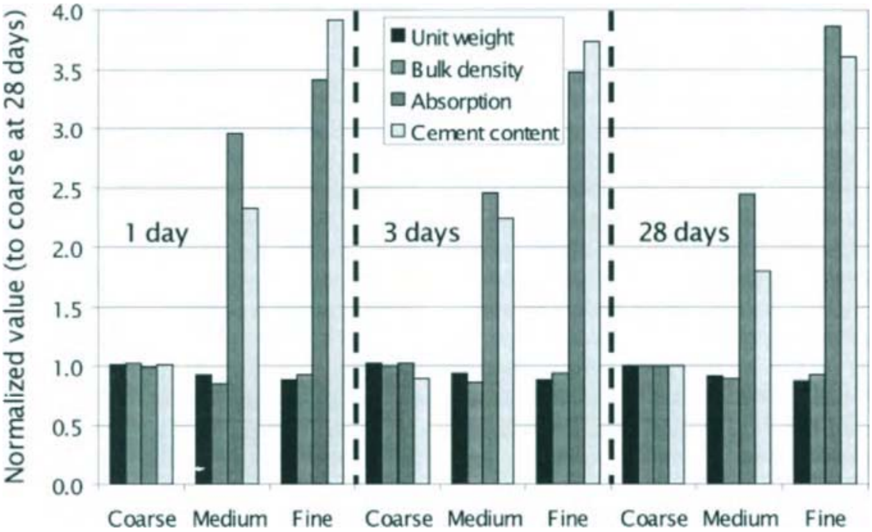

Figure 2: Properties of the recycled aggregates normalized to the coarse fraction crushed at 28 days.

The variation in the properties of the aggregates crushed at different ages is not significant. This suggests that the amount of the cement paste that was still adhered to the natural aggregates in each size fraction was uniform, regardless of the crushing age. The strength of the cement matrix, at the level of strengths studied here, has probably only a minor effect on the mode of crushing of the old concrete.

As a result of the similarity among the size distribution of the aggregates crushed at different ages, it was decided later on that separation of the recycled aggregates to the different size fractions is not needed for the production of the new concrete. Thus the recycled concrete was added as a whole to the mix (see Table 2).

3.2 Properties of new concrete made from recycled aggregates.

Fresh concrete

Properties of the new concrete are listed in Table 4. The bulk density of the fresh concrete made from natural aggregates as reference was in the range known for normal concrete (approximately 2400 kg/m^3). However, the concrete made from recycled aggregates was significantly lighter and was approximately 2150 kg/m^3 regardless of the cement type or crushing age. The lower density is the result of the lower density of the aggregates discussed before (2.6, 2.3 and 2.2 for the coarse, medium and fine crushed aggregates, while the density of the natural aggregates is 2.63-2.74 kg/m^3). In addition, an increased air content was observed leading also to additional reduction in the density of the fresh concrete.

Air content was calculated by the gravimetric method (ASTM C138). The results indicated normal air content for the reference concrete and increased air content of 4-5.5% for the concrete made from recycled aggregates. The reason for the increased air content is not clear. The air in the aggregate's voids is taken into account through the unit weight of the aggregate,

Table 4: Fresh and hardened properties of the new concrete

		White cement				Ordinary Portland cement			
		Reference	1 day*	3 days*	28 days*	Reference	1 day*	3 days*	28 days*
Bulk density (kg/m^3)		2462	2146	2170	2153	2463	2175	2145	2156
Slump (mm)		170	170	155	185	81	178	175	134
Calculated air content (%)		1.3%	5.4%	4.1%	5.0%	0.0%	4.8%	5.4%	5.6%
Compressive strength (MPa)	7 days	36.8	19.0	23.4	20.0	21.6	18.3	17.0	17.1
	28 days	42.1	24.1	30.5	29.1	34.6	26.6	25.8	26.8
	90 days	58.9	28.9	38.7	35.2		33.0	28.7	30.6
Flexural strength (MPa)		6.7	4.7	5.3	4.6	6.1	6.1	5.4	5.4
Splitting strength (MPa)		5.0	3.1	3.6	2.7	3.3	3.4	2.9	3.1
Modulus of elasticity (GPa)		23.1	11.4	13.7	11.5	22.7	13.6	12.6	12.8

thus the values above represent additional air that was entrapped in the concrete. Additional study is needed in order to better understand this phenomenon. It should be noticed that determination of the air content by the gravimetric method is very sensitive as minor changes in the unit weight of the aggregates may lead to large changes in the air content. Accurate determination of the unit weight is impossible due to difficulties in the determination of the saturated surface dry (SSD) state of the porous aggregates. Therefore the general trends of increased air content should be considered and not the exact values which may include an error of approximately ±1%. An increased air content is known also to occur in lightweight aggregates concrete (Wischers and Manns, 1974) that shows some similarities with the recycled aggregates from crushed concrete.

The slump of almost all the mixes was in the range of 135-185 mm (mostly ~175 mm) except the OPC reference mix that had an unexplained slump of 81 mm. The similar slump was achieved with a similar quantity of free water (see Table 2) indicating that water requirement for a given slump is not changed by the effect of aggregates type and crushing age. It should be noted however, that some quantities of natural sand were still needed for proper workability and cohesivity due to the insufficient amount of fines in the crushed aggregates.

Hardened concrete

Compressive strength: the compressive strength of the various mixes is shown in Table 4 for ages 7, 28 and 90 days. The differences between the two cements is shown when comparing the 28 compressive strength of the reference concretes; the one made from OPC was weaker by 18% compare to the white cement concrete. The effect of using the recycled aggregates was a reduction in the compressive strength of the concrete both when white cement or OPC was used. The reduction in strength was 30-40% when white cement was used, the maximum reduction was observed for the concrete made from aggregates crushed at 1 day. The reduction in strength was more moderate for the OPC (approximately 24%), regardless of the crushing age of the recycled aggregates.

No significant change was seen when comparing the effect of crushing age on the OPC concrete. However, significant changes were seen for the white cement concrete (see Figure 3). The white cement concrete with aggregates crushed at 1 day exhibited lower strength compare with the other ages of crushing. The aggregates crushed at 3 days exhibited the highest strength at all testing ages. The differences were moderate at 7 days and more pronounced at later ages (5% and 18% of differences between crushing age of 1 day and 28 days, for new concretes tested at 7 and 90 days, respectively).

4. DISCUSSION

The difference between the quality of the new cement matrix and the recycled aggregates seems to have an effect on the properties of the new concrete. Two opposing mechanisms seem to control the properties of the new concrete: (1) The mechanical properties of the recycled aggregates crushed at different ages and (2) The residual cementing ability of the unhydrated cement which remained in the recycled aggregates.

The mechanical properties of the aggregates crushed at different ages were not uniform as indicated by the compressive strength of the old concrete (see Table 1). Additional hydration

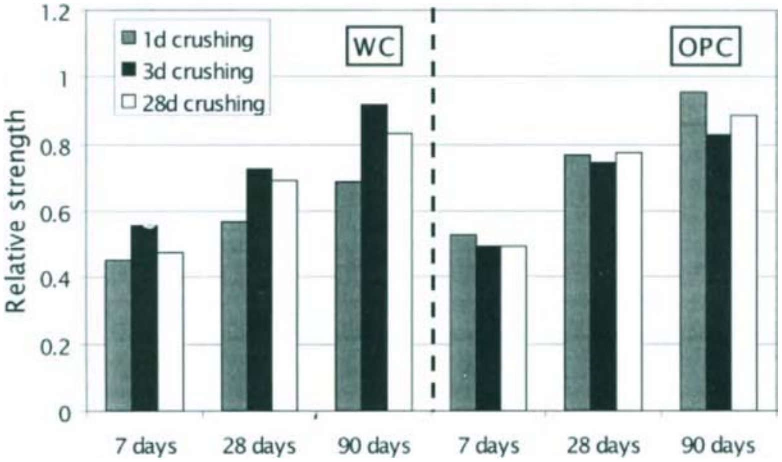

Figure 3: The compressive strength of recycled concrete relative to the reference concretes at different ages.

of the old cement in the recycled aggregates may somewhat improve the properties of the aggregates, mainly of those crushed at 1 day.

This effect is seen in the case where the cement matrix of the new concrete was stronger than the aggregates, as in the case of the new concretes prepared with the white cement. At the age of 7 days, when the cement matrix was relatively weak, there was no significant difference between the strength of aggregates crushed at 1 day or 28 days. At later ages (28 and 90 days) the new cement matrix became much stronger and the changes between aggregates properties were more significant; at 90 days the new concrete made from 1 day aggregates was weaker by 18% than the concrete made from aggregates crushed at 28 days.

For the recycled concrete crushed at 3 days, the strength of the old concrete at the crushing age together with the contribution of some unhydrated old cement lead to stronger concretes compared with the other concrete made from aggregates crushed at 1 or 28 days (see Figure 3).

The properties of the cement matrix of the new OPC concrete was relatively weak, thus no significant change could be seen between the various crushing ages, similar to the results from the white cement at 7 days.

5. SUMMARY AND CONCLUSIONS

1. The properties of the aggregates crushed at different ages were quite similar. Size distribution of the aggregates was the same for the three ages of crushing, as well as other properties such as absorption, unit weight, bulk density, cement content and crushing value of the coarse fraction. These observations indicate that at these strength levels and structure of the old concrete the aggregates that are made of it have quite similar

properties. Other properties, however, such as additional cementing properties or the mechanical properties of the fine fractions were not tested at this stage of the study.

2. Concrete made from 100% of the recycled aggregates was weaker than other concrete made from virgin aggregates at the same water to cement ratio. When the new concrete was made from the same type of OPC and the same water to cement ratio as of the old concrete, the strength reduction was of ~20% regardless of the crushing age of the old concrete. When white cement was used, the reduction was of 30-40% depending on the crushing age of the old concrete (the white cement provides with 20% higher compressive strength compare with the OPC concrete at the same water to cement ratio).
3. The properties of the aggregates made from the crushed concrete and the effect of the aggregates on the new concrete (strength, modulus of elasticity etc.) resemble those of lightweight aggregate concrete and similar attention should be given when dealing with this type of aggregates.
4. Two opposing mechanisms seem to affect the properties of the new concrete: the physical properties of the old concrete and the presence of unhydrated cement in the crushed concrete. These effects are seen when the new cement matrix is significantly stronger than the old concrete. Additional study in the next stages will clarify this assumption as well as determine the role of air entrapment and its effect on concrete properties.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Leaching behaviour of a chromium smelter waste heap

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This paper reports the results of geochemical sampling and modelling of leachates from a chromite ore processing residue (C.O.P.R.) pile under rainwater infiltration. The waste pile is located in the north of England and consists of 800 000 m^3 of waste. The pH of fresh leachate is similar to that of a solution in equilibrium with portlandite $Ca(OH)_2$, which is a major constituent of the waste. The in-gassing of $CO_2(g)$ causes the pH of the leachates to drop along the drainage ditch and calcite precipitation to occur. The extent of in-gassing is dependent upon the flow rate within the drainage ditch. The dissolution of solid solutions containing residual chromate is likely to control chromate concentrations within the leachate.

1. INTRODUCTION

Chromite ore processing residue (C.O.P.R.) is produced during the manufacture of chromates and dichromates. C.O.P.R has been used widely as landfill material in England, Japan, West Germany and the United states (McKee, 1988). This may be problematic as C.O.P.R contains potentially harmful elements, including Cr and Al.

C.O.P.R is formed by a high temperature process and in common with other high temperature mineral residues, its composition is dominated by alkaline and alkali earth oxides. Therefore it is at disequilibrium under normal atmospheric conditions. To attain equilibrium with its new environment it undergoes compositional evolution. Evolution also occurs because of removal of waste components by leaching.

This paper reports an investigation of the leaching behaviour of C.O.P.R under rainfall infiltration. The alteration of leachate by reaction with the atmosphere is also reported. Precipitation and clogging problems within the site drainage system are also discussed.

2. SITE DESCRIPTION

The site covers an area of around 8 hectare in the north west of England (Breeze, 1973). Some 800, 000 m^3 of C.O.P.R. was produced at the site from 1893 until 1966 (Alderson et al. 1981; Breeze, 1973). Reclamation during the late 1960's was based on work carried out by Breeze (1973) and Gemmell (1972, 1973, and 1974). These workers reported that both chromate level and pH reduction was needed for the establishment of healthy vegetation.

Hence the waste was capped with gravel (20 cm) as a capillary break and topsoil (15 cm), to provide a rooting medium. The site was landscaped to direct infiltration into a drainage system at the site margins. The site is now covered with grass, and has trees around its margins. However some grassed areas show signs of distress and there are frequent leachate overflow incidents due to precipitates blocking the drainage system.

3. CHROMATE MANUFACTURE

The process used at the site (the high lime process) is described by Alderson et al. (1981), Breeze (1973), Theopold (1989), Shreve (1967) and Bidstrup (1951). The initial stage of the process was the conversion of insoluble chromite ore into water-soluble chromate. Roasting a mixture of chrome-iron ore, with sodium carbonate and lime at 1100°C for several hours produced sodium chromate. The lime acted as a mechanical separator allowing oxygen to react with the chromite and sodium carbonate (1).

The sodium chromate produced was extracted in water, and the residue discarded. The sodium chromate was then converted into sodium dichromate by reaction with sulphuric acid.

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2 \qquad (1)$$

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O \qquad (2)$$

The high lime process does not extract all the chromium. The residue which was disposed of on-site, contains unreacted chromite ore and unextracted chromate. The sodium sulphate formed as a by-product had no commercial value during the period the factory operated and it was also disposed of on-site

4. FIELD INVESTIGATION

Leachates from the C.O.P.R. waste pile were sampled at their point of first emergence and two points further down the drainage ditch (Figure 1).

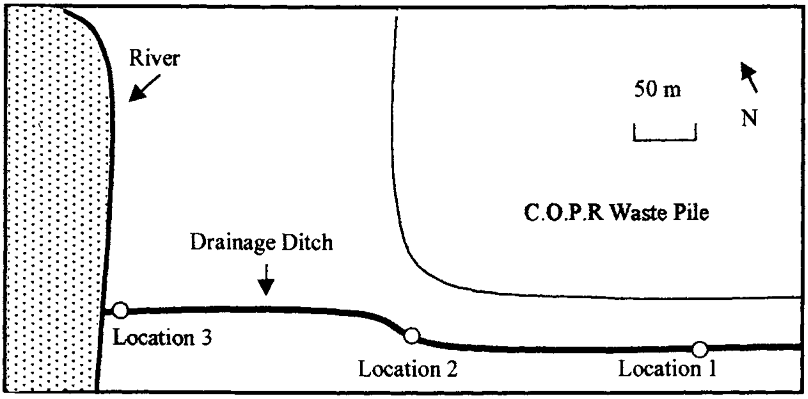

Figure 1 Diagram showing the location of sampling points.

Comparison of the leachate chemistry at these points was expected to show how the leachate interacts with the atmosphere. A preliminary investigation was carried out to determine the appropriate sampling frequency for the study. Insitu measurements including pH, conductivity and temperature were collected on a daily basis for two weeks. As variations were minor sampling on a weekly basis was adopted.

The pH, temperature and oxygen reducing potential (ORP) were all measured on-site using a Whatman multi tester (the pH meter uses a two-point calibration and is accurate to +/- 0.2 pH, whereas temperature is accurate to +/- 1 °C and ORP is accurate to +/- 5 mV). The conductivity data was also measured on-site using a Jenway conductivity meter (Model 4070).

Separate samples were collected in 30 ml high-density polyethylene bottles for total cation analysis, anion analysis and for total carbon dioxide analysis in the laboratory. The samples were filtered on-site at 0.45 μm (Whatman Puradisc disposable filter). All sample bottles were filled ensuring no headspace, to minimise the ingress of CO_2. The samples taken for total cation analysis were acidified on-site using 5% nitric acid (ASTM, 1982). Samples were transported to the laboratory in a coolbox.

5. LABORATORY METHODS

Samples were stored at 5 °C and filtered at 0.2 μm prior to analysis. Total cation analysis for 15 cations (Cr, Ca, Na, K, Mg, Zn, Pb, Ni, Cd, Mn, Fe, Cu, Al, Sr and Ba) was carried out using Inductively Coupled Atomic Emission Spectroscopy (ICP-AES). Anion levels (sulphate, nitrate, chloride and fluoride) were determined using Ion Chromatography (IC) on a Dionex® DX-100 system. Batches of cation and anion analyses were carried out every 3 weeks. Total CO_2 analysis was carried out using a flow injection method (Hall and Aller, 1992) (samples were analysed within 24 hours of collection).

6. GEOCHEMICAL MODELLING

Two software packages (SOLMINEQ.88 and MINTEQA2) were used to speciate the leachate solution and find the saturation indices (SI) of minerals in the leachate. MINTEQA2 version 3.11 was also used to speciate chromium (SOLMINEQ.88 does not have thermodynamic data for chromium).

The Saturation Index (SI) of a mineral is the logarithm of the ion activity product (IAP) divided by the solubility product (K_{sp}) ($SI = \log IAP/K_{sp}$). Positive SI values indicate that a mineral is oversaturated and precipitation is possible, whereas negative values indicate that it is undersaturated and will tend to dissolve. An SI of zero indicates that a solution is in equilibrium with a mineral phase. Modelling was used to identify the mineral(s) controlling the chemistry of the leachate emerging from the waste, and the reactions between leachate and atmospheric CO_2.

The input data for SOLMINEQ.88 included the pH, temperature and Eh, total cation data (Ca, Na, K, Mg, Zn, Pb, Ni, Cd, Mn, Fe, Cu, Al, Sr, Ba), anion data (SO_4^{2-}, NO_3^-, Cl^-, F^-) and total CO_2 data.. The total CO_2 data was entered as total inorganic carbon. The same input data was used the MINTEQA2 program along with Cr data. Aqueous Cr was assumed to be chromate and hydroxyl levels were found by assuming unit activity for H^+. CrO_4^{2-} ranged from 3.4×10^{-4} to 2.5×10^{-4} *M*.

7. LEACHATE CHEMISTRY RESULTS

The dominant cations at the leachate emergence (Location 1) were Na^+ (14.2 to 9.6 mM) and Ca^{2+} (3.27 to 2.71 mM) (Figure 2) and the dominant anions were SO_4^{2-}(6.3 to 5.9 mM), CO_3^{2-} (3.2 to 0.9 mM) (Figure 3) and CrO_4^{2-}. The fluids were hyperalkaline (Figure 4) (i.e. the leachate emergence pH was between 10.3 and 11.5). The pH at the leachate emergence fell towards the end of the sampling period. The pH also fell as the leachate moved along the open drainage ditch. During the sampling period, there was a visually observable increase in the flow rate around 25/09/99, which correlates with an increase in rainfall recharge into the waste. The leachate was precipitating calcite (identified by XRD analysis) at the emergence point and along the length of the drainage ditch.

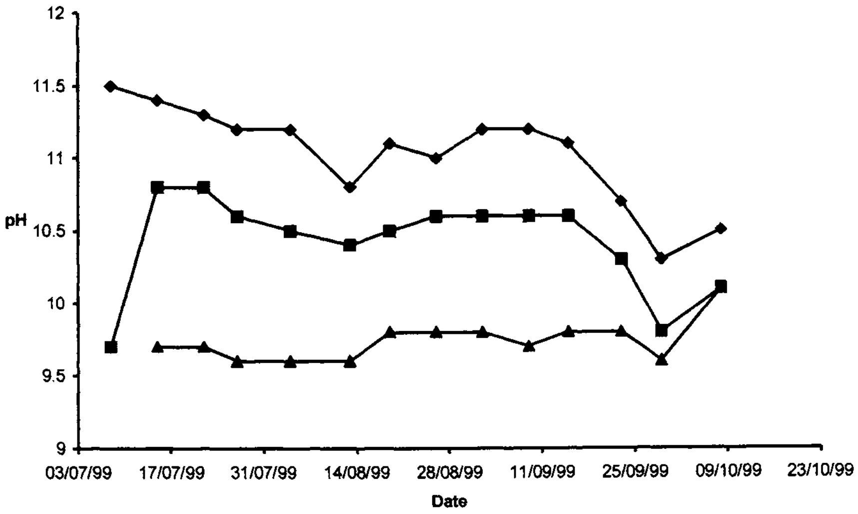

Figure 4 pH of the leachate at emergence (diamonds) the second sampling point (squares) and the third sampling point (triangles).

The total CO_2 content of the leachate increased as the fluid moved along the drainage ditch (Figure 3) (usually mostly between the leachate emergence and location two). After peaking in August 99 the total CO_2 concentration at all three locations fell towards the end of the sampling period.

The concentration of calcium at all locations remained fairly constant (Figure 2). With only a slight increase in concentration towards the end of the sampling period. However, the concentration of calcium decreased along the drainage ditch (mostly between the leachate emergence and location two).

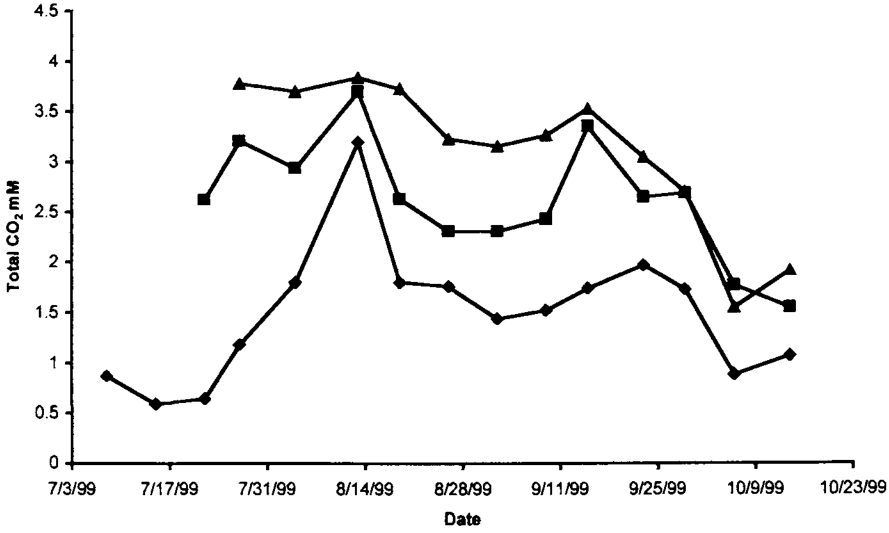

Figure 3 Total CO_2 of the leachate emergence (diamonds) the second sampling point (squares) and the third sampling point (triangles).

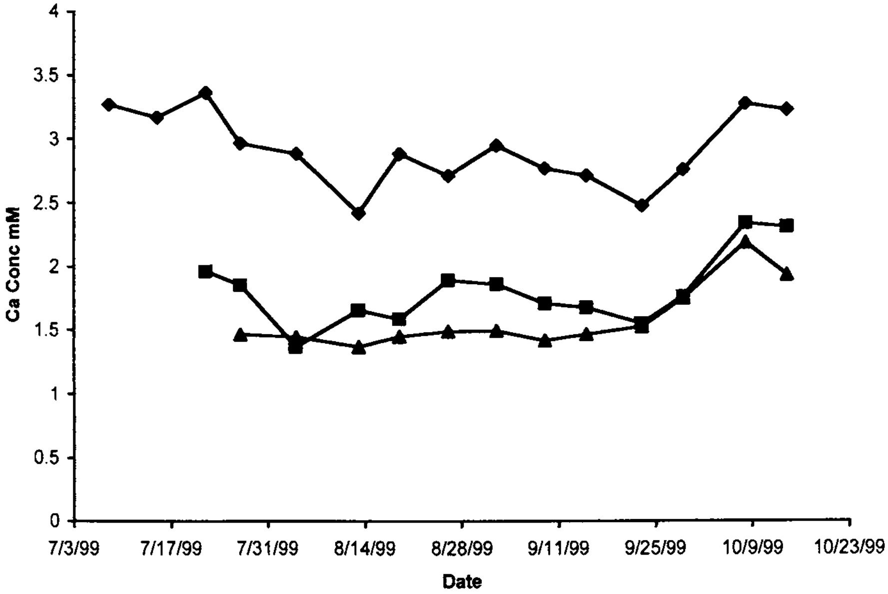

Figure 2 The concentration of calcium in the leachate emergence (diamonds) the second sampling point (squares) and the third sampling point (triangles).

8. MODELLING

The saturation indices for the minerals likely to be controlling leachate chemistry, were found by the geochemical modelling programmes (SOLMINEQ.88 and MINTEQA2) (Table 1).

Table 1 Mineral SI calculated by SOLMINEQ.88 and MINTEQA2.

Mineral	Location 1 SI			Location 2 SI			Location 3 SI		
	Av	Min	Max	Av	Min	Max	Av	Min	Max
Brucite $Mg(OH)_2$	0.8	-0.7	1.8	-0.4	-1.8	0.6	-2.0	-2.2	-1.4
Portlandite $Ca(OH)_2$	-4.3	-6.1	-3.3	-5.8	-7.2	-5.0	-7.3	-7.7	-6.9
Hydromagnesite $Mg_5(CO_3)(OH)_2.4H_2O$	2.1	0.9	2.7	1.4	-0.4	3.3	-1.3	-2.2	-0.3
Ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}.25H_2O$	0.2	-0.7	0.9	-0.8	-1.6	-0.2	-1.7	-1.8	-1.5
Calcite $CaCO_3$	2.5	2.3	2.5	2.4	2.3	2.4	2.2	2.1	2.3
Aragonite $CaCO_3$	2.3	2.2	2.4	2.2	2.1	2.3	2	2	2.1
Dolomite $CaMg(CO_3)_2$	5	4.6	5.7	5.1	4.6	5.5	4.8	4.6	4.9
Disordered Dolomite $CaMg(CO_3)_2$	3.5	3	4	3.5	3.2	3.9	3.1	2.9	3.2
Gibbsite $Al(OH)_3$	0.3	-0.1	1.4	1.0	0.5	1.6	1.5	1.1	1.7
Gibbsite Amorphous $Al(OH)_3$	0.7	0.3	1.7	1.3	0.9	1.9	1.8	1.1	2
Gypsum $CaSO_4.2H_2O$	-1.3	-1.6	-1.0	-1.6	-1.8	-1.3	-1.5	-1.6	-1.3
Magnesite $MgCO_3$	0.9	0.6	1.1	1.1	0.9	1.4	0.8	0.7	0.9
Barium Chromate $BaCrO_4$	-0.9	-1.1	-0.6	-0.9	-1.2	-0.8	-0.96	-1.2	-0.9
CalciumChromate $CaCrO_4$	-4.6	-4.8	-4	-4.9	-5	-4.8	-5	-5.1	-5

8.1. Leachate Emergence

The geochemical modelling showed that portlandite $Ca(OH)_2$ was strongly undersaturated in the emergent leachate. Ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}.24H_2O$ ranged from slightly oversaturated to slightly undersaturated. Gypsum $CaSO_4.2H_2O$ was undersaturated, whereas calcite $CaCO_3$ and aragonite were saturated in the emergent leachate.

Brucite $Mg(OH)_2$ was usually slightly oversaturated at the leachate emergence. Dolomite $CaMg(CO_3)_2$ and disordered dolomite were oversaturated (dolomite was generally more oversaturated than disordered dolomite) and magnesite $MgCO_3$ and hydromagnesite $Mg_5(CO_3)(OH)_2.4H_2O$ were saturated.

Amorphous gibbsite $Al(OH)_3$ and crystalline gibbsite were both oversaturated at the leachate emergence (amorphous gibbsite was more saturated than gibbsite). Gibbsite approached equilibrium during some of the study (i.e. SI = 0).

At the leachate emergence barium chromate was only slightly undersaturated, whereas calcium chromate, potassium chromate, sodium chromate, magnesium chromate, strontium chromate and lead chromate were all highly undersaturated.

8.2. Drainage Ditch

Calcite $CaCO_3$, aragonite and magnesite $MgCO_3$ remained saturated along the drainage ditch, and dolomite $CaMg(CO_3)_2$ and disordered dolomite remained oversaturated. Hydromagnesite $Mg_5(CO_3)(OH)_2.4H_2O$ was saturated at the second sampling point, and was undersaturated by the third sampling point. Both amorphous and crystalline gibbsite become increasingly oversaturated along the drainage ditch, whereas chromate bearing phases remained undersaturated. Hydroxide phases (portlandite and brucite) became increasingly undersaturated.

9. DISCUSSION

9.1 Leachate Emergence

The high pH of the leachate indicates that the minerals controlling its chemistry are likely to be hydroxides of the alkaline earth metals which are known to present within the waste, produced by the high temperatures utilised in chromate manufacture. Portlandite will probably have been produced as lime (CaO) hydrated on exposure to water during sodium chromate extraction.

The pH of the leachate in the drainage ditch is well below the equilibrium pH of portlandite which is 12.4 (Schramke, 1992) and portlandite is undersaturated. However the leachate in the drainage ditch does not emerge directly from the waste. Recent extensive cleaning of the drainage ditch has reduced the retention time of the leachate before it enters the drainage ditch. Near location 1 the pH of this fresher leachate is 12.3 - 12.4. Therefore it is likely that the pH of the leachate is controlled by portlandite and that previous pH measurements were affected by reaction with carbon dioxide in the soil, before leachate entered the drainage system.

Calcite and aragonite are both oversaturated in the leachate. It is likely that this is due to reaction with soil $CO_2(g)$ as the leachate passes from the waste to the drainage system. They remain oversaturated, as precipitation is initially kinetically inhibited (Lorah and Herman, 1988). Calcite is also likely to form within the waste as it is exposed to $CO_2(g)$ in the pore gas and in dissolved in infiltrating rainwater.

Brucite will probably have formed as MgO within the waste hydrated on exposure to water during the extraction of sodium chromate. Brucite should remain in the waste where the pH is maintained above 12 by portlandite (i.e. where the pH in is too high for brucite dissolution). Areas within the waste that have been preferentially exposed to rainwater infiltration may have reduced buffering capacity. Within such areas brucite dissolution could occur.

Dolomite and disordered dolomite are oversaturated at the leachate emergence. Dolomite formation within the waste is unlikely, because of kinetic inhibition. Low temperature formation of dolomite is rare and studies have shown that the kinetics of dolomite precipitation strongly favour high temperatures (Arvidson and Mackenzie, 1999; Sibley et al. 1994). Although magnesite and hydromagnesite are both slightly oversaturated they are also unlikely to form within the waste for kinetic reasons. Magnesite is approximately ten times supersaturated in the oceans and precipitation has not been observed (Langmuir, 1997). Hydromagnesite is rare and tends to be found only in evaporative environments (Langmuir, op. cit.).

Gibbsite and amorphous gibbsite are oversaturated at the leachate emergence indicating the possibility of precipitation. However the precipitation of gibbsite from solution may take some weeks (Hem and Robertson, 1967; Smith and Hem, 1972). Hence gibbsite will only form within the waste where the residence time of the infiltrating rainwater is relatively high.

C.O.P.R contains residual chromite ore and unleached chromate. The residual ore is unreactive and it is likely that unleached chromate is the main source of chromate within leachates, although the chemical speciation of this solid phase chromate remains unknown. Previous authors (e.g. Breeze, 1973) have suggested that unleached chromate is present as calcium chromate. However, Weng et al. (1994) and James (1994) did not find calcium chromate salts in soils derived from COPR (XRD Analysis). Also calcium chromate is probably too soluble to remain in the waste for very long (see saturation indices in Table 1). The data from this study indicates that barium chromate is only slightly undersaturated within the leachate emergence. Any barium chromate in the waste is likely to be present as a solid solution with calcium chromate, with a slightly lower solubility than pure barium chromate (Fallman, 1997). Hence the chromate levels in the leachate maybe controlled by the dissolution of this phase.

9.2. Leachate Evolution

Data from the sampling points along the drainage ditch show how the leachate evolves while exposed to the atmosphere. The SI for portlandite was negative, while those for brucite and ettringite became negative down the flow path (as pH fell). In contrast calcite remained oversaturated, although saturation decreased slightly along the flow path. This is consistent with the observed precipitation of calcite along the drainage ditch.

Hyperalkaline fluids absorb $CO_2(g)$ and precipitate calcite when exposed to atmospheric conditions (Khoury et al. 1985). This proceeds according to the following reaction scheme taken from Clark et al. (1992).

$$CO_{2(g)} \rightarrow CO_{2(aq)} \quad (3)$$

$$CO_{2(aq)} + OH^- \rightarrow HCO_3^- \quad (4)$$

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \quad (5)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (6)$$

Once $CO_2(g)$ is taken into solution at high pH (Eq 3) aqueous CO_2 undergoes reaction with OH^- (Eq 4). This consumes OH^-, which lowers the pH. Subsequent dissociation of HCO_3^- to CO_3^{2-} produces H^+, which further lowers the pH of the solution. CO_3^{2-} then reacts with Ca^{2+} to precipitate calcite. Variations in the flow rate influence the extent to which reaction (3) occurs in the soil and along the drainage ditch, and hence the amount of pH reduction between sampling points. The reduction in pH observed within the drainage ditch could also be achieved by mixing with run-off from the surrounding area.

10. CONCLUSIONS

A chromite ore processing residue (C.O.P.R.) waste pile has been investigated by leachate sampling and geochemical modelling. The fresh leachate collected after extensive cleaning of the drainage system has a pH which is compatable with the equilibrium pH of portlandite. Dissolution of solid solutions containing residual chromate are likely to control chromate concentrations in the leachate (CrO_4^{2-} levels ranged from 3.4 x 10^{-4} to 2.5 x 10^{-4} *M*). The evolution of the hyperalkaline leachates in the drainage ditch results from in-gassing of $CO_2(g)$ and subsequent calcite precipitation (causing extensive problems with drainage system blockages). The extent of in-gassing and calcite precipitation depends on the flow rate in the drainage ditch (higher flow results in less in-gassing and less precipitation).

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Use of sulphate containing sieve sands in building materials

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This paper discusses the results of a research project into the use of the fine fractions of demolition wastes for the production of building materials. Often, these wastes contain high amounts of leachable sulphate, which prevents application in an unbound form due to the criteria of the Dutch Building Materials Decree. In order to reduce sulphate leaching, solidification processes were developed to chemically immobilise the sulphate in the form of ettringite. Two types of building materials were developed: a road base construction material, and a concrete product for use as so-called mega blocks. A number of hydraulic binders have been tested for these purposes. For both types of application, products can be made that fulfil both engineering demands and leaching criteria.

1. INTRODUCTION

Sieve sands, the fine fractions of demolition wastes (particle size < 10 mm), contain relatively high amounts of easily leachable sulphates (3-6 wt%), originating predominantly from plaster and plaster board [1]. Therefore, these sands cannot be applied in unbound form, according to the criteria of the Dutch Building Materials Decree (BMD). The maximum allowable immission for sulphate equals 100 000 mg/m^2 for unbound building materials and 45 000 mg/m^2 for bound building materials, according to the BMD. The aim of the research is to immobilise the sulphates (chemically) and stabilise the waste (physically) with cement and/or additives, so that the product fulfils the criteria of the BMD and can be utilised as a building material. Two types of applications are being developed: a road base construction material, and concrete products ("mega-blocks"). These two types of application require different approaches with respect to the development of the stabilisation process, since the demands on product properties such as compressive strength are different.

2. IMMOBILISATION OF SULPHATE

Immobilisation of sulphate can be achieved by chemical binding in the form of ettringite and other calcium sulpho aluminates. The formation of ettringite proceeds according to the following gross reaction equation:

$$3\ CaO + Al_2O_3 + 3\ CaSO_4 + 32\ H_2O \rightarrow 3\ CaO.\ Al_2O_3.\ 3\ CaSO_4.\ 32\ H_2O$$

In order to attain a sufficient degree of sulphate binding, a hydraulic binder is needed, which contains at least the stoichiometrically required amounts of calcium and aluminium for ettringite formation. The chemical form of the reactants will be of importance for the reaction. Note that from cement chemistry, it is known that tricalcium aluminate (C_3A) reacts with calcium sulphate to form ettringite. In cement matrices ettringite can be found in the pores. Besides chemical binding, physical binding ("shielding") is an important mechanism in the reduction of leaching. Obviously the extent of physical binding is correlated to the pore structure of the material (porosity, pore size distribution, tortuosity).

3. EXPERIMENTAL METHODS

The extent to which sulphate is chemically bound in the products was determined by means of a modified version of the standardised Dutch availability test (NEN 7341), which is carried out on finely ground material (<125 μm) that is subjected to acidified water. The adapted test comprises three subsequent steps, instead of two steps as in the standard test. In the first step the pH is not controlled (own pH of the material, for cement bound materials usually pH > 10). In the second and third steps the pH is controlled at pH=7 and pH=4, respectively, by the addition of 1 M nitric acid. In the first step the sulphate bound in the form of calcium sulphate leaches, but ettringite is stable and doesn't leach. Apart from this, the own pH of the material corresponds in practice to the actual leaching conditions that the material is subjected to in an application. In the second step (pH=7) ettringite disintegrates, and the sulphate trapped as ettringite leaches. In the third step (pH=4), the even more stable sulphate species leach.

The actual leaching from the prepared products was studied with the Dutch diffusion test (NEN-7345) with a modified replacement scheme. The diffusion test (tank leaching test) is carried out by placing a sample in a tank which is filled with acidified leachant. The leachant is replaced according to a specified time schedule. The replacement scheme was modified with respect to the standard test in order to shorten the test: the standard test lasts for 64 days, whereas the above tests were carried out in a period of 25-days.

4. CHARACTERISATION OF WASTE MATERIALS

In this research, three types of sieve sand were used: two relatively highly contaminated sorting sieve sands (A and B) and a relatively "clean" breaker sieve sand (C). Two types of washing sludge were used, a relatively highly contaminated sludge from washing of sorting sieve sand (D) and a relatively "clean" sludge from washing of demolition debris (E). By developing applications for these washing sludges, the washing processes become economically more attractive. All sieve sands and washing sludges had been subjected to column leaching tests, and none fulfils the criteria of the Building Materials Decree with respect to sulphate leaching. For the production of concrete products, a number of other waste materials with coarse grain sizes were applied, in order to modify the grain size distributions. These materials (F-I) included granulated reclaimed asphalt pavement, slag from steel production, contaminated gravel and ballast from railways. From availability leaching tests it appeared that these coarse materials contain negligible amounts of leachable sulphate compared to the sieve sands and washing sludges. The results of leaching tests with the sieve sands and the sludges are given in table 1.

Table 1
Results characterisation tests

Waste material	A	B	C	D	E
type	sorting sieve sand	sorting sieve sand	breaker sieve sand	washing sludge sieve sand	washing sludge dem. debris
moisture content [wt%]	16.3	17.7	14.4	46.6	47.2
loss on ignition [wt%]	3.9	ND	2.8	13.7	4.5
sulfate availability [g/kg]					
step 1 (own pH)	30 (96%)	15 (79%)	3.3 (49%)	47 (63%)	4.7 (43%)
step 2 (pH=7)	1.7 (5.4%)	2.3 (15%)	2.8 (42%)	18 (25%)	6.1 (55%)
step 3 (pH=4)	1.4 (4.5%)	1.1 (7.3%)	0.64 (10%)	3 (4.1%)	2.1 (19%)
sulfate content [mg/kg]	31	19	6.8	74	11

5. DEVELOPMENT OF SAND-CEMENT STABILISATIONS

5.1 Preliminary results

Sorting sieve sand (A from table 1) was used for development of a sand-cement stabilisation layer. The first trials to develop stabilised products with Portland cements and high-alumina cements (mixtures 1-4) showed promising results [2]. The main results of these previous tests are included in table 2. Sufficient compressive strengths could be achieved by adding 10% m/m of cement with respect to sieve sand (a value of 3-5 MPa after 28 days is required). In leaching tests it was shown that sulphate could be chemically bounded to a significant extent. Sulphate leaching at the own pH of the material in the first step of the 3-step availability test was only 25-50% of the total sulphate availability, compared to virtually 100% in unstabilised sieve sand. It is noted that in mixtures 1 and 2, only about 50% of the required amount of aluminium necessary for complete transformation of sulphate into ettringite was actually present.

5.2 Recipe development

New mixture compositions (mixtures 5-10) based on Portland, high alumina and blast furnace slag cements were defined. For economical reasons (high costs of binder), mixture types 3 and 4 were abandoned, while in mixtures 5 and 6 the same binders as in mixtures 1 and 2 were used in higher contents. It is noted that also in these mixtures, the amount of aluminium present was still lower than stoichiometrically required for complete conversion of sulphate into ettringite. A different binder was tested in mixture 7, whereas combinations of binders were tested in mixtures 8 and 9. The idea behind mixing was to fulfil stoichiometric requirements for ettringite formation, while keeping the amount of expensive binders low. Mixture 10 is in fact a further optimisation of mixtures 2 and 6.

Test pieces were prepared which were tested in 25-day diffusion tests. From these tests, sulphate immissions after 1 year were calculated according to the methods prescribed by the Dutch Building Materials Decree. Also, the first step of the 3-step availability tests was performed with each mixture. The results are shown in Table 2.

Mixtures 5 and 6 show a considerable increase in compressive strength compared to mixtures 1 and 2, and a slight decrease in the relative amount of sulphate leached at the own pH. For mixtures 5 and 6, the sulphate availability at the own pH is about equal, which indicates that the extent of chemical binding is about the same. The extrapolated immissions are well below the upper allowed limit of 45000 mg/m^2. Mixture 6 shows a remarkably lower immission than mixture 5. This could be explained by improved physical binding, which is in agreement with the considerably higher compressive strength of mixture 6.

The compressive strengths of mixtures 7 and 8 are relatively high. However, the sulphate leaching levels are also relatively high, both in the availability tests and in the diffusion tests. Apparently, binder V is not able to chemically bind the sulphate to as high an extent as the other binders, though the stoichiometric constraints for ettringite formation are fulfilled in

Table 2

Results of recipe development for sand stabilisation layer

Mixture	Binder type	Binder content [wt%]	Al present / Al required	Compressive strength [MPa]*	Calculated immission [mg/m^2]**	Sulphate leached at own pH [mg/kg]
1	I	10	0.41	3.1	ND	12,000 (44%)
2	II	10	0.47	3.0	ND	11,000 (50%)
3	III	10	3.6	4.7	ND	8,700 (32%)
4	IV	10	4.5	5.2	ND	9,600 (26%)
5	I	20	0.73	6.5	20,000	12,000 (35%)
6	II	20	0.95	10.4	5,200	11,000 (39%)
7	V	15	1.4	10.3	30,000	16,000 (55%)
8	II+V	15	1.1	12.9	25,000	15,000 (52%)
9	II+IV	10	1.3	7.1	12,000	8,100 (27%)
10	II	17	0.83	9.1	5,400	5,300 (19%)

* After 28 days

** Extrapolated from diffusion tests; upper allowed limit = 45,000 mg/m^2

terms of elemental composition. This may be explained by different chemical forms of aluminium and calcium.

Mixture 9 has a higher compressive strength than both mixtures 2 and 4 (which contain the two binders that are also present in mixture 9). Also, the extent of sulphate leaching in the first step of the availability test is lower than for mixtures 2 and 4. Apparently, blending causes a synergetic effect. This might be explained in terms of chemical reactions between the ingredients.

The compressive strength of mixture 10 lies between the compressive strengths of mixtures 2 and 6 (which contain the same binder), as may be expected on the basis of the binder content. However, it is striking that the amount of sulphate leached in the first step of the availability test is remarkably lower for mixture 10 than for mixtures 2 and 6, for which the leached amounts are about equal. This seems to point to differences in chemical forms. Despite this, the immissions from the diffusion tests are about equal for mixtures 6 and 10.

5.3 Conclusions

The results show that it is possible to develop a product that fulfils both mechanical and environmental demands. Application of binder II results in efficient immobilisation of sulphate. Application of binder V results in high compressive strengths, but also in less efficient immobilisation.

6. DEVELOPMENT OF CONCRETE PRODUCTS

6.1 Waste materials

In order to prepare products with concrete properties, a number of combinations of waste materials, hydraulic binders and additives were studied. The very first trials pointed out that a sufficient compressive strength (~30 MPa) can not be achieved on the basis of sieve sand, washing sludge and cement alone. Therefore, it was decided to add coarse materials to the mixtures, in order to obtain a more favourable particle size distribution. In order to keep the economy of the process attractive, a number of waste materials were selected to fulfil this role. Two basic mixture types were defined: a relatively "clean" mixture, containing relatively low sulphate levels, and a relatively "contaminated" mixture. The "clean" mixtures consisted of sieve sand C and washing sludge E (see table 1) as fine materials, in a ratio 80:20 wt/wt (wet basis). Two also relatively clean coarse waste materials (G and H) were added as a coarse material. The ratio of coarse to fine materials was 40:60 wt/wt. Though this ratio was not the optimum from an engineering point of view, it was considered an acceptable compromise between engineering demands and commercial interests, since the objective of the project was to immobilise sieve sand and washing sludge. The "contaminated" mixtures consisted of sieve sand A/B, washing sludge D and reclaimed asphalt pavement (F) (see table 1) as fine materials, in a ratio of 40:10:50 wt/wt (wet basis). A more contaminated coarse waste material (I) was added to the mixtures. The ratio of coarse and fine materials was again 40:60 wt/wt.

6.2 Hydraulic binders

Four types of hydraulic binder mixtures were investigated. The binder mixtures were based on blast furnace slag cement, Portland cement and high alumina cement. The blast furnace slag and Portland cements that were used were modified compared with commercially available cements. The cements were applied in mixtures with bentonite and a waste material (ash) from an incineration process. The addition of bentonite was based on the results of previous experiments, which indicated that bentonite might be able to adsorb sulphate. The addition of the ash was based on stoichiometric considerations for ettringite formation, since the material is rich in aluminium and calcium. Mixing of binders was also based on considerations concerning the stoichiometry for ettringite formation.

6.3 Recipe development

The ingredients used in the various mixture compositions are given in table 3. First, mixture 14A was prepared, based on a mixture of cements. The purpose was mainly to determine the amount of binder necessary to attain a sufficiently high compressive strength. However, the mixture turned out to harden too fast for appropriate handling to be possible. Therefore the mixture was prepared once more, but with a different type of cement. The mixture hardened fast again, though somewhat slower than mixture 14A, and the compressive strength was slightly higher. Since the compressive strengths were disappointing, the next mixture to be prepared (15) was prepared with a higher cement content. Though the compressive strength was still not high enough, the other mixtures were prepared with the same binder content as mixture 15, because higher cement contents were considered uneconomical. Furthermore, the workability decreased with increasing cement content.

Comparison of mixtures 11 and 12 shows the lowering effect of bentonite on the compressive strength. The workability of mixture 11 was much worse than the workability of mixture 12.

The results for mixture 13 show that with a mixture of cement and ash, a quite reasonable compressive strength can be obtained, even though the cement content was only 235 kg/m^3 (at a total binder content of 469 kg/m3).

Table 3

Mixture compositions concrete product development

Mixt.	Binder	Content [kg/m^3]	Waste materials	Coarse materials	Density [kg/m^3]	Compressive strength [MPa]	Workability
11	V+ bent.	416	C / E	G	2015	15	low
12	V	439	C / E	G	2110	28	reasonable
13	I + ash	469	C / E	G	1980	21	reasonable
14A	II + III	332	C / E	G	2100	12	sets too fast
14B	I + III	346	C / E	G	2135	16	sets fast
15	I + III	430	C / E	G	2090	20	sets fast
16	V + bent.	433	C / E	H	2100	19	low
17	V + bent.	416	B / D / F	I	2070	19	low
18	V	454	B / D / F	I	2145	27	reasonable
19	V	440	A / D / F	I	2110	19	reasonable
20	II + III	458	B / D / F	I	2150	21	low

Coarse material H may be expected to have latent hydraulic properties. Comparison of mixtures 11 and 16 reveals that the use of coarse material H instead of G results in a higher compressive strength.

When mixtures 16 and 17 are compared (same binder), it appears that the mixture of waste materials has only little influence on the compressive strength. This seems to be confirmed by the results for mixtures 15 and 20, although the type of cement that was used was different. On the other hand, a comparison of mixtures 18 and 19 shows that the type of sieve sand can have a remarkable effect on the compressive strength.

6.4 Leaching tests

The mixtures were subjected to availability tests and shortened diffusion tests. Mixtures 11 and 14 were abandoned for the leaching tests, because the compressive strengths were too low. Also, mixture 20 was abandoned, because of the bad workability of the mixtures based on combinations of binders II and III. However, in order to study the influence of the addition of binder III on the leaching of sulphate, mixture 15 was subjected to leaching tests.

From the diffusion tests, sulphate immissions after 1 year were calculated according to the methods prescribed by the Dutch Building Materials Decree. The results of the leaching tests are given in table 4.

It should be noted that in none of the tested mixtures stoichiometric limitations existed for ettringite formation, at least in terms of elemental composition. The mixtures contained 10-20 times the stoichiometrically required amount of aluminium for complete conversion of sulphate to ettringite (the sulphate contents of the mixtures are lower than the mixtures for sand-cement stabilisations, while the cement contents are higher). Of course, the chemical form of the reactants should also be taken into consideration.

By comparing mixtures 12 and 16 it appears that the addition of bentonite results in increased sulphate leaching (immission) in the diffusion test. However, the first step of the availability test shows about equal amounts of leaching, both absolutely and relatively. This indicates that the extent of chemical binding is about equal, and that the differences in the immissions are due largely to differences in physical bonding. Unfortunately the influence of coarse material H (mixture 16) instead of G (mixture 12) on the sulphate leaching can not be derived.

Table 4
Results of leaching tests

Mixture	Sulphate leached at own pH [mg/kg] *	Immisssion** [mg/m^2]
12	1400 (49%)	1900
13	1700 (24%)	1200
15	1500 (17%)	830
16	1400 (43%)	3000
17	2400 (45%)	2000
18	2100 (38%)	830
19	3900 (51%)	970

* Relative to estimated content

** Upper allowed limit: 45,000 mg/m^2

However, both G and H contain insignificant amounts of leachable sulphate. Furthermore, components from material H used in mixture 16 may participate in the hydration reactions, resulting in a higher compressive strength. It may be expected that this leads to a *de*creased sulphate leaching. The apparent *in*creased leaching may be related to a different product structure, which affects the extent of physical bonding (note the lower density and compressive strength). Apparently, any increased adsorption on bentonite (if occurring at all) cannot counteract this.

By comparing mixtures 12 and 15 it is concluded that with a binder based on a mixture of binders I and III, the extent to which sulphate is bound increases, when compared to a mixture based on binder V. The relative amount of sulphate leached in the first step of the availability test is very low, as is the immission calculated from the diffusion test.

The leaching from mixture 13 is of the same order of magnitude as from mixture 12, despite the low cement content in mixture 13. The relative amount leached in the first step of the availability tests is significantly lower. This may indicate that higher amounts of ettringite are formed, which may be caused by the chemical form of the reactants. The results show the potential of this binder type, based partly on a waste material, for stabilisation practices.

Comparison of mixtures 18 and 19 reveals the differences in leaching levels between products based on sieve sands A and B. The increased leaching from mixture 19 can be ascribed both to the higher sulphate content of sieve sand A, and to differences in the physical structure of the product (note the differences in compressive strength).

Mixtures 16 and 17 show the effect of using a relatively "clean" or a relatively "contaminated" mixture of waste materials. In the first step of the availability test the relative amounts leached are about equal, though the absolute amount is higher in mixture 17. However, the results from the diffusion test show a lower immission from mixture 17 ("contaminated") than from mixture 16 ("clean"). This may be caused by differences in the physical structure. A number of samples of the diffusion test with mixture 16 were analysed for heavy metals. The results indicated that the leaching levels of the heavy metals will remain below the allowed levels.

6.5 Conclusions

It has been shown that all tested mixtures can easily fulfil the demands of the BMD. The calculated sulphate immissions are far below the upper allowed limit of 45000 mg/m^2. The mixture composition to be applied will therefore be determined largely by the mechanical demands on the product. It can be concluded that binder V (mixtures 12 and 18) results in the highest compressive strength and density. Furthermore, a combination of binder I and ash results in a very reasonable compressive strength (mixture 13), considering the low content of cement (50% of the total binder content). The leaching levels are also acceptable and well within the regulatory limits. In general however, the compressive strengths of the mixtures are not high enough for application as concrete, though the results are very promising. Also the densities are lower than those of "normal" types of concrete. Therefore it is concluded that further optimisation of the mixture compositions is necessary.

7. FUTURE WORK

For further optimisation, three new mixtures will be prepared. Mixture 12 will be further optimised by adding a plasticizer. For mixture 13, the ratio of cement to ash will be increased while maintaining the total amount of binder equal. Mixture 18 will be optimised by adjusting the ratio of coarse and fine materials. To obtain a higher compressive strength it would be useful to prepare mixtures with coarse material H instead of G. However, G has a negative economical value whereas H costs money. Because of this it is recommended to develop mixtures based on G.

The research into the preparation of road foundation materials has led to the development of a suitable binder for sulphate containing sorting sieve sand. The application of the developed product will be tested in a demonstration project. This field test is in preparation at the time of writing. Within this project, a road will be constructed in which a part of the foundation layer consists of stabilised sieve sand. The actual leaching from this road part will be monitored for a period of a year, by collecting leachate samples at various points. The recipe of mixture 10 will be the basis for the field test. Since a different batch of sieve sand will be used than the ones used here, the optimum recipe to be applied will be determined on the basis of further testing on a laboratory scale.

The recipes for preparation of concrete will be further optimised, in order to arrive at the desired compressive strength of 33 MPa. On the basis of the results obtained so far it is expected that the preparation of products with favourable mechanical properties will be possible in an economically viable way. The leaching from the optimised products will be measured in diffusion tests. Further evaluations will show the economical viability of the products.

The effects of changes in mixture compositions on the leaching behaviour are not in all cases predictable. It would be desirable to gain more insight into the relation between the properties of the waste materials and the applied binders, in order to optimise the development trajectory for new products. In the ideal case, it should be possible to determine the amount and type of binder to be applied from a straightforward characterisation of the waste material(s), in combination with the desired product properties. Further research into the formation of ettringite in these kind of mixtures is desired.

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Observations of Leaching of Low Concentration Contaminants From Alternative Aggregates in Road Constructions

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Many materials resulting from domestic and industrial activity could be used as a replacement for natural aggregates in road construction. Environmental protection organisations have raised concern over the potential for resultant contamination of ground and surface water systems. The leaching properties of a selection of aggregate materials are being examined in a testing programme designed to progressively simulate the real conditions within a road construction. The testing programme is described, illustrative data is presented and initial conclusions are drawn.

1. INTRODUCTION

Road construction and bulk fill consume vast quantities of raw materials. In the UK, the majority of these materials are currently obtained from natural rock sources. Such quarrying operations result in many adverse environmental impacts such as disturbance of the landscape, increased traffic, noise and dust and the generation of derelict land.

At the same time, industrial and domestic activities generate vast quantities of materials that require management or disposal. Many such materials have been shown to form mechanically suitable replacements for traditional aggregates within a road construction either in an unbound form or with the addition of simple binders [Nunes, 1997]. Examples of such materials include power station ashes, blast furnace and steel slags, incinerator ashes, foundry sands, mining and quarrying spoil and construction and demolition materials [Sherwood, 1995; Dawson et al., 1995]. The University of Nottingham has been carrying out research in this field for nearly a decade, and has developed a system for predicting mechanical performance [Nunes, 1997]. This system allows for appropriate treatment (e.g. by addition of low levels of cement, lime, bitumen, etc) where mechanical performance is not otherwise adequate.

The use of both primary and alternative aggregate materials has come under scrutiny by environmental protection organisations, such as the Environment Agency in the UK. Although the use of alternative aggregates holds a dual environmental benefit to society by cutting waste volumes requiring disposal and reducing the quarrying of primary aggregate, concerns have been raised over the potential of such materials to contaminate ground and surface water systems. Some alternative aggregates, inherently or as a consequence of the process from which they are sourced, contain environmentally undesirable elements or compounds [Baldwin et al., 1997]. It is therefore necessary to demonstrate that no, or an acceptably low, risk of contamination to the environment would result from usage of aggregate materials in road construction.

The UK Ground Water Regulations introduced in 1998 [DOE, 1998] (to implement the European Community Directive 80/68/EEC, "Protection of groundwater against pollution caused by certain dangerous substances") imposes very strict limits for discharges of substances to groundwater. If this legislation is to be rigidly enforced then the road construction industry may be required to perform environmental risk assessments for the use of any alternative or conventional construction material in order to be able to demonstrate an acceptably low risk.

2. MATERIAL ASSESSMENT STRATEGY

To assess the true leaching potential of aggregate materials when used in a road construction scenario, an assessment of any contamination should be made based upon realistic end use conditions. The insitu properties of the material must be understood in order to correctly interpret leaching test data. A programme of testing has been carried out at the University of Nottingham to identify whether the following insitu material conditions influence leaching.

- Material grading
- Degree of compaction
- Insitu hydraulic regime
- Combination with other aggregates or binders, for mechanical reasons, which may alter the leaching conditions.

The overall aim of the research is to develop a methodology by which any material can be simply assessed to determine suitability for use as a road construction material. For materials which are found to be unsuitable for use in an unbound condition a strategy for applying appropriate simple binder treatments is also being developed.

3. TESTING STRATEGY

A vast number of leaching tests exist for a wide variety of applications. Many of these tests originate from the hazardous waste management industry where contaminant concentrations are often many orders of magnitude above those present in any form of potential construction material. The applicability of such leaching tests to aggregate materials is therefore in some doubt. The purpose of the programme was to progress through a tiered testing strategy from simple index tests towards tests which assess materials in conditions more simulative of the material conditions and hydraulic regime of a road construction. For materials that were found to be unsuitable for use in an unbound condition, the use of binders to limit contaminant release was investigated.

The experimental programme included:

- Solids analysis as major and trace element compositions.

- Maximum availability leaching tests using the draft CEN standard PrEN 12457 “Compliance test for leaching of granular wastes and sludges” [CEN TC 292, 1996].
- Large scale advection testing using horizontal permeameters at natural hydraulic gradients.
- Small scale advection testing using vertical permeameters at high hydraulic gradients.
- Tank leaching tests using materials in different physical arrangements (e.g. loose, compacted and compacted and bound).
- Outdoor, full-scale lysimeter tests to simulate real conditions within a road construction.

Details of the test methods used in the experimental programme are described below along with a list of materials used in the research.

3.1. Materials

The range of alternative and conventional aggregates and binders that were selected for assessment within the research are summarised in Table 1.

Table 1. Alternative and Conventional Aggregates and Binders for Assessment.

Material Source	**Material**
Power Station	Pulverised Fuel Ash Furnace Bottom Ash Flue Gas Desulphurisation Gypsum
Incinerator Ash	Municipal Solid Waste Incinerator Ash Sewage Sludge Incinerator Ash
Metallurgical Slag Products	Air-Cooled Blast Furnace Slag Steel Slag Granulated Blast Furnace Slag Ground Granulated Blast Furnace Slag
Mining and Quarrying Spoil	China Clay Sand Minestone (waste rock associated with coal mining)
Foundry Sand	Greensand (sand with a clay binder) Alkali Phenolic Binder Foundry Sand
Vehicle Tyres	Crumbed Rubber
Road Maintenance	Black Top Planings
Conventional Aggregate	Limestone Granite
Binders	Cement Cement Kiln Dust Lime

3.2. Assessment of the Composition of the Solid Material

Initially the material solid compositions were analysed using X-Ray Fluorescence Spectrometry together with a number of other techniques on the more complex materials. Determining the composition of the materials enabled some knowledge of each material to be gained and gave an indication of what contaminants may be of concern. However, simply because a certain element or compound is present in a material does not imply that all or any of it will leach out under real conditions. It is therefore necessary to carry out leaching tests on the materials.

3.3. Compliance Leaching Test

The first phase of the leaching test programme utilised the draft European Standard (PrEN 12457 Leaching) "Compliance test for leaching of granular waste materials" [CEN TC 292, 1996]. This test involves reducing the particle size of the material so that 90% is less than 4mm and 100% is less than 10mm. A two stage batch agitated leaching test is carried out using distilled water at liquid to solid ratios of 2:1 for 6 hours and then 10:1 for a further 18 hours. This test was designed to be a simplification of more detailed characterisation tests. However, the conditions are much harsher than those that would be found in a real road construction and it was anticipated, therefore, would produce what could be considered to be pessimistic results.

3.4. Effect of Material Particle Size

The second phase of the testing programme was developed to investigate the effect of the material particle size and grading on leaching. In the UK road construction situation, materials are generally used at a defined grading with particles of up to 60mm in diameter. It was expected that the larger particles would release components at a slower rate than the crushed material that was used in the compliance testing. This is due to the lower surface area to volume ratio and the longer diffusion pathway, through the solid, along which the released components would need to move before entering the leachant.

A tank leaching test was utilised for this section of the programme. The procedure was adapted from the NEN 7345 Tank Leaching Test Procedure [NEN 7345, 1993]. A 2kg sample of material and distilled water leachant, were used at a 10:1 liquid to solid *mass* ratio. The leachant was unagitated and samples were taken periodically over 64 days. A schematic diagram of the test equipment is shown in Figure 1.

3.5. Effect of Material Compaction

The third testing phase was designed to investigate the effect of material compaction on leaching. When materials are used in a road construction they will nearly always be compacted. Compaction has the effect of reducing the pore space and the material permeability and therefore reducing the volume of leachant that comes into contact with the material.

To examine diffusive leaching from compacted aggregates a tank leaching test has again been used. The material sample was compacted at the optimum moisture content for compaction, to the maximum dry density, into a cylindrical mould 150mm in diameter and 75mm high. The sample was then cured, by sealing it within a plastic bag to prevent loss of moisture, for a period of 90 days to allow any pozzolanic reactions to be initiated. The samples are then tested as described in Section 3.4 above, but with a liquid to solid ratio of 10:1 by *volume*. The volumetric ratio was chosen to account for the variations in density of the materials which in the field would result in different material masses being required to perform the same filling task.

The effects of compaction on advective leaching are assessed using permeameter apparatus. Two types of permeameter are being used and the choice of apparatus is dependant upon the permeability and the particle size of the individual compacted material. For the higher permeability and larger particle sized aggregates, a large horizontal permeameter is being used. This apparatus is the standard equipment for testing aggregate permeabilities in the laboratory [DoT, 1990] and is illustrated in Figure 2. The sample is compacted into a box 1m x 0.3m x 0.3m and leachant is forced through the sample under a hydraulic head. For relatively low permeability and small particle size aggregates a DoRLaP (Double Ring Laboratory Permeameter) apparatus [Birtwhistle, 1997] is being used. This apparatus holds a cylindrical sample 100mm in diameter with heights varying between approximately 20mm and 150mm. The chosen sample height depends upon the material permeability. This apparatus enables high hydraulic heads to be applied to the sample.

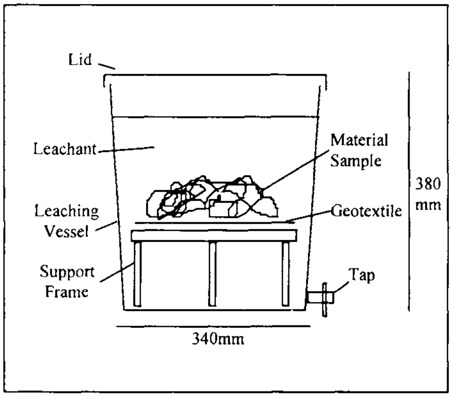

Figure 1. Tank Leaching Test Equipment.

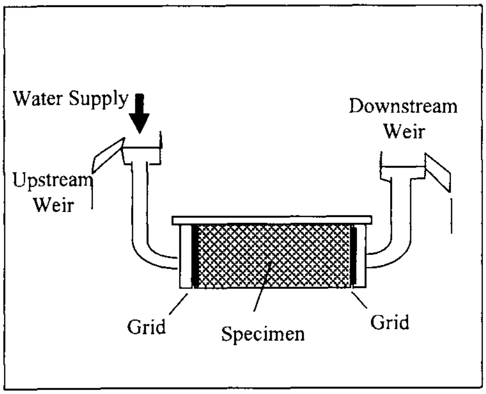

Figure 2. Large Horizontal Permeameter.

3.6. Effect of Material Binding

To achieve satisfactory mechanical performance for use within a road construction some aggregate materials require the addition of binders (such as cement, lime, bitumen or alternative binders such as granulated blast furnace slag or pulverised fuel ash). The addition of binders may however, effect the leaching properties of the materials in a number of ways:

- Reducing the pore space and permeability within the compacted aggregate;
- Coating the surface of the individual particles and hence reducing contact between the material and the leachant;
- Altering the pore water chemistry, such as the pH and therefore effecting the mobility of many components of the materials.

The effects of material binding are, therefore, assessed using the compliance, tank and permeameter leaching tests previously described.

3.7. Full Scale Testing

To enable the laboratory test results to be more accurately related to potential insitu road conditions nine large scale field tests have been established. The completed lysimeter field is shown in Figure 3. These test cells are $1m^2$ in surface area and have an overall depth of approximately 0.6m. The completed cells have a gravel drainage layer in the base upon which a 350mm layer of test material was compacted and another at the top. The latter allows water to enter but prevents rain impact and 'spatter'. Nine different aggregates or mixtures have been used at realistic gradings and degrees of compaction. The test cells have been exposed to the natural environment and the precipitation (leachant) percolating through the lysimeters is sampled, the volumes recorded and chemical analyses performed. The principal difference between the lysimeter construction and that of the real pavement is that the rain water can fall directly onto the permeable surface. This is similar to the pavement during construction, but not as surfaced.

Figure 3. Photograph of the Lysimeter Field.

4. RESULTS

The results and discussion presented in the following sections of this paper have been drawn from initial results of the compliance testing, the tank leaching tests on materials in the various conditions (i.e. full grading, compacted, bound) and preliminary data from the lysimeter field. Illustrative data is presented to enable the discussion of the effect of material condition (such as grading and compaction) and binding on leaching. The appropriateness of each test for assessing insitu leaching is also addressed.

Due to the sensitivity of the issues discussed in the following sections of this paper, it is, at present, not possible to disclose which sets of data have been obtained from which test material. Once the full data set is available sensible comparison of results will be possible. Until that time it would be imprudent to possibly prejudice one materials performance relative to another on the basis of incomplete data. It is hoped that the full data will be available at the time of the conference presentation, perhaps allowing disclosure at that time.

Some illustrative data on which the discussion is based is presented in Tables 2 to 5. The leaching data is expressed as cumulative milligrams released per kilogram of test material. The pH and conductivity measurements are those directly measured from the test leachates without any correction for the particular liquid to solid ratio exhibited in the individual test. Table 2 presents some data for the leaching of sodium and copper from 3 test materials in the compliance test, the tank test with the material sample at the full grading and the tank test with a compacted material sample. Table 3 presents some data to illustrate the effect of an alkali binder whilst Table 4 addresses the use of an inert binder. Table 5 presents some preliminary data from the lysimeter tests.

Table 2. Leaching of sodium and copper from 3 test materials in the compliance and tank leaching tests.

	Sample	Material A			Material B			Material C		
Test	Time of Sampling	pH	Na mg/kg	Cu mg/kg	pH	Na mg/kg	Cu mg/kg	pH	Na mg/kg	Cu mg/kg
CEN	6 hrs	6.7	712	6.1	6.8	6.9	<0.01	6.8	1500	<0.01
	24 hrs	7.8	754	8.1	6.5	12.6	<0.05	3.4	1538	0.11
Tank L	6 hrs	11.8	1975	29.2	6.0	1.2	<0.05	6.3	1675	<0.05
	24 hrs	11.9	2089	35.8	6.3	2.7	<0.05	6.9	2102	<0.05
	4 days	11.7	1757	34.8	6.7	4.8	0.06	7.4	2148	<0.05
Tank C	6 hrs	7.9	435	2.8	6.6	1.1	<0.03	6.6	593	<0.03
	24 hrs	10.1	635	4.7	6.7	1.7	<0.03	6.8	1147	<0.03
	4 days	10.4	1013	7.4	7.0	3.2	0.029	7.1	1951	0.05

CEN = Compliance test (see Section 3.3)
Tank-L = Tank test with uncompacted material at full grading (see Section 3.4)
Tank-C = Tank test with compacted material at full grading (see Section 3.5)

Table 3. Comparison between leaching of Material B and Material B with an alkali binder in a tank leaching test using sodium and aluminium as example analytes.

	Sample	Material B			Material B + alkali binder		
Test	Time of Sampling	pH	Na mg/kg	Al mg/kg	pH	Na mg/kg	Al mg/kg
Tank C	6 hrs	6.6	1.1	<0.12	11.5	27.6	0.8
	24 hrs	6.7	1.7	<0.12	11.9	33.9	2.4
	4 days	7.0	3.2	<0.12	11.9	44.1	5.1

Tank-C = Tank test with compacted material at full grading (see Section 3.5)

Table 4. Comparison between leaching of Material A and Material A with an inert binder in a tank leaching test based on pH and conductivity measurements.

Sample		Material A		Material A + inert binder	
Test	Time of Sampling	pH	Conductivity µS	pH	Conductivity µS
Tank C	6 hrs	7.9	623	7.5	118
	24 hrs	10.1	993	10.0	250
	4 days	10.4	1455	10.6	467

Tank-C = Tank test with material compacted at full grading (see Section 3.5)

Table 5. Comparison between lysimeter, compliance and tank leaching test data based on pH and conductivity measurements.

Sample		Material A		Material D		Material E	
Test	Time of Sampling	pH	Conductivity µS	pH	Conductivity µS	pH	Conductivity µS
Lysi	1	12.1	14350	9.0	3930	8.2	308
	2	10.4	22900	7.9	3580	8.3	490
CEN	6 hrs	6.8	5210	7.9	2610	6.3	192
	24 hrs	8.5	1450	6.5	425	6.5	112
Tank L	6 hrs	11.4	2790	7.4	690	8.6	68
	24 hrs	11.6	3060	8.1	954	8.5	75
	4 days	11.7	3220	8.7	1192	8.3	73
Tank C	6 hrs	9.3	623	-	-	-	-
	24 hrs	10.3	993	-	-	-	-
	4 days	10.6	1455	-	-	-	-

Lysi = Lysimeter data
CEN = Compliance test (see Section 3.3)
Tank-L = Tank test with material at full grading (see Section 3.4)
Tank-C = Tank test with material compacted at full grading (see Section 3.5)

5. DISCUSSION

The initial research hypothesis that was being investigated was that:
"As the testing conditions approach similarity to realistic road construction conditions, (i.e. real grading, compaction, binding) the leaching of the components of the construction materials will reduce and the rate of leaching will decrease".

The expected results based on this hypothesis were that the largest releases (mg/kg) would occur during the compliance leaching test. The tank leaching tests were expected to extract less than the compliance leaching test. The tank test results were expected to produce ranked results with the tests on the full graded material releasing more and at a faster rate than the tests on the same material in a compacted condition, and with the bound samples producing the least release and at the slowest rate. The lysimeters developed in this study were designed to give an approximation to realistic insitu (during construction) conditions and to enable a comparison to be made to the different leaching tests.

Initially the data was examined to investigate the effect of material condition as proposed by the hypothesis. The data for the leaching of sodium and copper presented in Table 2 illustrates some of these observations. For the leaching of sodium it can be seen that for Material B the hypothesis is correct in that the greatest amount is leached during the compliance test, with less being leached during the loose material tank test and similarly less in the compacted tank test. However, for Materials A and C the situation is very different. For these materials more sodium is leached in the loose material tank test than in the compliance test. For the tank leaching tests the hypothesis is followed in that there is less release from the compacted samples that the loose samples. Similar patterns are exhibited for the leaching of copper although the degree of variation differs.

This disagreement with the original hypothesis implied that a factor other than the material condition was also influencing the leaching process. As it is a well known fact that pH affects the solubility and hence the leaching characteristics of most elements and compounds, the influence of the test pH was examined. Again drawing on the data presented in Table 2, amongst others, it can be seen that there is some considerable variation in the pH between the different test methods when testing the same material. It is often observed that the quantity leached follows patterns that are influenced by the particular pH exhibited during that test. The test pH may be influenced by numerous factors. A change in pH may *cause* alterations in the leaching patterns of other components, but may also be the *effect* of the leaching of other components. Some factors which may be influencing the test pH include the leaching time, material size reduction or preparation method, contact and mixing with air during the test or the result of other co-ion effects.

Table 3 presents data for a material bound with an alkali binder. It was hypothesised that binder treatment would inhibit leaching by reducing material permeability, adjusting the pH of the pore water and by chemical interactions. In the case presented in Table 3 it can be seen that the bound sample actually leaches more sodium and aluminium than the unbound sample. In this particular case, the bulk material (Material B) in question contains only a small proportion of leachable elements and therefore the increase in leaching from the bound sample must have originated from the binder itself. Similar data for a material containing a higher proportion of leachable species was not available at the time of the paper preparation, however, it is expected that in such cases the alkali binders will produce a resultant reduction in leaching.

Table 4 presents data for a material bound with an inert binder. Only pH and conductivity data is presently available but it can be seen that although the pH is changing at a similar rate in both tests, the conductivity from the bound sample is significantly less than that from the untreated material sample. This implies that there is less leaching occurring.

As there is considerable variation between the results obtained from different test methods, the question arises as to which test is most simulative of the insitu road leaching environment. Table 5 presents pH and conductivity data for 3 lysimeters along with compliance and tank leaching test data for the same test materials. It is obvious from this table that the pH of the lysimeter leachates more closely resembles that of the tank tests rather than the compliance test. Such a correlation is not so obvious for the conductivity measurements. This does however have important implications on the suitability of certain test methods for application to road construction material assessment.

6. CONCLUSIONS

Initial conclusions that can be drawn from the results presented here are that:

- The total amount and the rate of leaching is affected by the material condition (i.e. grading, compaction and binding).
- However, leaching may be more significantly controlled by the pH of the leaching environment.
- Although binders have the potential to reduce leaching they also have the potential to introduce further, and sometimes more significant, contaminants to the system.
- Any prediction of leaching potential must incorporate a robust prediction of likely pH. Tank testing may provide such a technique, but this will require further investigation before the limitations of such an approach can be fully appreciated.

Wider conclusions that can be drawn are that:

- For laboratory leaching tests to give a realistic estimation of potential insitu leaching, the pH of the test should simulate that of the end-use environment. The application of a simple compliance test may therefore not always be suitable.
- If water enters the road construction environment, the pH of the construction material and resultant leachate may be important for two reasons:
    a) for itself (i.e. the influence of a change in pH on the surrounding environment).
    b) because of the effect on the leaching of other components of the materials.
- The type of aggregate and/or binder used should be matched to the environment of usage. For example, in environments that are sensitive to alkalinity, such as acidic heathland, the use of alkali aggregates and binders should be restricted.

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Waste Materials in Construction
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The use of MSWI (Municipal Solid Waste Incineration) bottom ash as aggregates in hydraulic concrete

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The general objective of this study is the innovative use of MSWI bottom ash as aggregates for hydraulic concretes, especially in ready to use concretes and in prefabrication.

As first, a complete physical, chemical and mineralogical characterization of a MSWI bottom ash provided by the company YPREMA, was undertaken, in relation to requirements of the experimental standard XP P18-540 (« Aggregates for hydraulic concretes») and environment aspects (composition and concentration of the potential pollutant by fractions). Following this characterization, the aptitude of the MSWI bottom ash to be used with the hydraulic cements (CEM I and CEM III) was evaluated in mortars. The experience with different additions allowed a meaningful treatment protocol to be defined, especially by addition of silica fume which shows a relatively fast set of the mixture and good mechanical resistance. Concretes were first formulated using a CEM I with silica fume. Concretes with a silico-alumineous fly ash, a pouzzolan cement CEM IV/B and a diatomaceous powder were then studied. Results show the possibility of obtaining plastic B20 and B25 concretes with a partial or total replacement of natural aggregates by MSWI bottom ash.

1. INTRODUCTION

The annual municipal solid waste production in the European Union is currently estimated at 150 millions tons, of which about 20% is incinerated, producing close to 9 millions tons of MSWI (municipal solid waste incineration) bottom ash, most of which has to be disposed of in landfill. This quantity must increase again with the growth of the municipal solid waste production. Otherwise, the progressive closing of landfill sites imposed by the future European regulations, coming into effect in 2002 in France, will induce an increasing recourse to MSWI and to other uses as alternative to the storage of these products. In these conditions, a very important problem of MSWI bottom ash elimination rises in very short term.

The present study is a part of an European project « Mashroad » (contract BRST-CT97-5150) whose general objective is the innovative use of MSWI bottom ash in road techniques, with a part relative to the possibilities of use of the MSWI bottom ash as aggregates for hydraulic concrete, especially for concrete ready to the use or for the prefabrication.

The studies undertaken by Nectoux and al. (1995)[1,2] on the use of the MSWI as aggregates in hydraulic concretes concluded that the mineralogical properties of the MSWI bottom ash should be taken into account in the criteria for use of MSWI bottom ash while their incorporation in cement matrix, considering the possible formation of expansive mineral whose evolution is to be monitored. Otherwise, it appeared that the MSWI bottom ash is usable only in partial substitution as sand and as coarse aggregate. The concrete using 25% MSWI bottom ash as aggregates has physical and mechanical properties analogous to a reference concrete. However, it is to be noted that these MSWI bottom ashes were aged for 5 years and that the minerals and the unstable soluble salts could be leached or recrystallized in more stable forms during this period. Others attempts (E. Jansegers, 1997)[3] consisted to study the use of MSWI bottom ash as aggregates in the production of hollow concrete blocks. Their results are promising and revealed good mechanical strength when MSWI bottom ash was used as about the third of the aggregates in weight.

A study made by P.J. Wainwright and al. (1983)[4] consists to determine the compressive strength, the flexural strength and the elastic module of the concretes made with Edmonton's MSWI bottom ash for which the varied cement contents and water to cement ratios were used. Generally speaking, the mechanical properties of these concretes are rather close to a classic concrete with a cement content of 220 kg/m^3 and a water to cement ration of 0,73.

Coutaz and al. (1997)[5] showed that the use of MSWI bottom ash as coarse aggregate in classic concretes induce some disorders because of the reaction with cements. This reaction produces a great decrease of mechanical strength and generates cracking which leads even to the complete disintegration of samples, mainly due to the reaction between metallic aluminum present in MSWI bottom ash and the alkalis present in cement. The proposed treatment to face this problem is to immerse the MSWI bottom ash in a bath of sodium hydroxide during 15 days in order to destroy all trace of aluminum. Using so treated MSWI bottom ash, a concrete of 25MPa at 28 days were obtained with 50% MSWI bottom ash and 50% natural coarse aggregate and a concrete of 20MPa at 28 days with 100% of MSWI bottom ash. No cracking was observed and the concretes had a good resistance to drying - immersion cycles.

In this study, the MSWI bottom ash is provided by the French company YPREMA.

2. CHARACTERIZATION OF THE MSWI BOTTOM ASH

2.1. Physical characteristics

2.1.1. Specific gravity, coefficient of absorption and water content

The MSWI bottom ash was separated in two fractions 0/5 mm and 5/20 mm, in order to constitute a sand and a coarse aggregate for later tests on concretes.

The specific gravity, the coefficient of absorption, the porosity and the water content were determined according to the standard NF P18-555 for the sand and the standard NF P18-554 for gravels. The results are given in Table 1.

The fact that the specific gravity of the fraction 5/20 mm is appreciably higher than that of the fraction 0/5 mm and that the water content and the coefficient of absorption of the later are higher could be attributed to the higher content of glass and metals in the fraction 5/20 mm.

Table 1
Specific gravity, coefficient of absorption and water content of the MSWI bottom ash

Characteristics	Fraction 0/5 mm	Fraction 5/20 mm
Real specific gravity (t/m^3)	1.88	2.26
Moistened specific gravity (t/m^3)	2.08	2.34
Water content (%)	22.1	11.5
Coefficient of absorption (%)	10.6	3.2

2.1.2. Cleanness, flakiness index and fine particles content

The cleanness of the MSWI bottom ash was determined by measuring the equivalent of sand according to the standard NF P18-598 for sands and by indicating the superficial cleanness according to the standard NF P18-591 for gravels. The results are given in Table 2.

Table 2
Measure of cleanness and equivalent of sand

	Fraction 0/5 mm	Fraction 5/20 mm
Equivalent of sable : E_S (%)	31	-
E_{SV} (%)	35	
Superficial Cleanliness : P	-	17,2

2.1.3. Grading

The grading curves were determined on fractions 0/5 mm and 5/20 mm by sieving. The results are reported in Figure 1.

The grading curve of the fraction 0/5 mm is extended on the fine fraction, indicating the significant presence of very fine particles in the MSWI bottom ash, while that of the fraction 5/20 mm is less continuous and irregular. It is to be noted that the crumbling of the material during the sieving operation gives to this result an indicative character.

2.2. Mechanical characteristics

From the mechanical point of view, three tests were undertaken in order to characterize the MSWI bottom ash : test Los Angeles according to the standard NF P18-573 to value the resistance to shocks (fraction 10/14 mm), Micro-Deval test according to the standard NF P18-572 to value the resistance to the attrition (fraction 4/6,3 mm) and test Los Angeles made after frost-thaw cycles according to the standard NF P18-593 to determine the frost sensibility of the MSWI bottom ash. The results are indicated in Table3.

2.3. Mineralogical characteristics

2.3.1. Mineralogical analysis by X-ray diffraction (XRD)

The mineralogical analysis by XRD was made on the fractions 0/5 mm and 5/20 mm. The minerals detected in the MSWI bottom ash are reported in Table 4.

2.3.2. Observations under optic microscopy with reflexive light

The examination under optic microscopy in reflected light were made on polished sections of the fraction 0/5 mm. Many fragments of glass with very variable dimension, some metallic fragments, some polyphases particles and a few agglomerates around these particles were observed.

On the fraction 5/20 mm, the MSWI bottom ash is composed of a lot of glass and metal, many agglomerates around the particles which are mixed with C_2S and lime, and some fly ash particles.

2.3.3. Observations under scanning electronic microscope(SEM)

The examination under scanning electronic microscope (SEM) of the fraction 0/5 mm show the presence of calcite, lime, calcium silicate (C_2S), crystallized slag, some hydrates, glass, ettringite and gehlenite.

In the fraction 5/20 mm, many metallic fragments in the form of iron oxides, iron chlorides and metallic iron were detected.

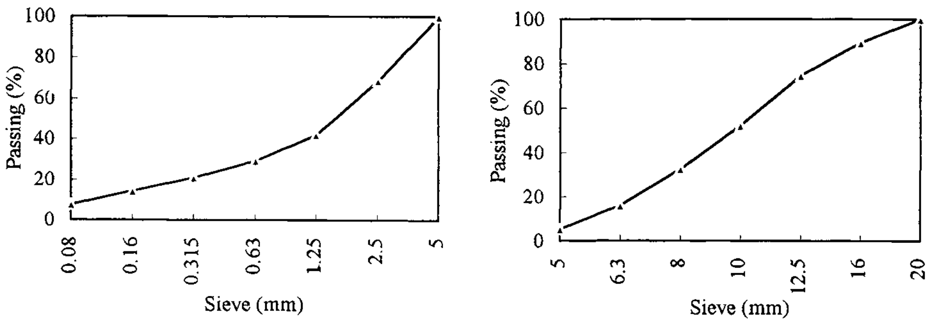


Fig. 1: Grading analysis of the fractions 0/5 and 5/20 of the MSWI bottom ash

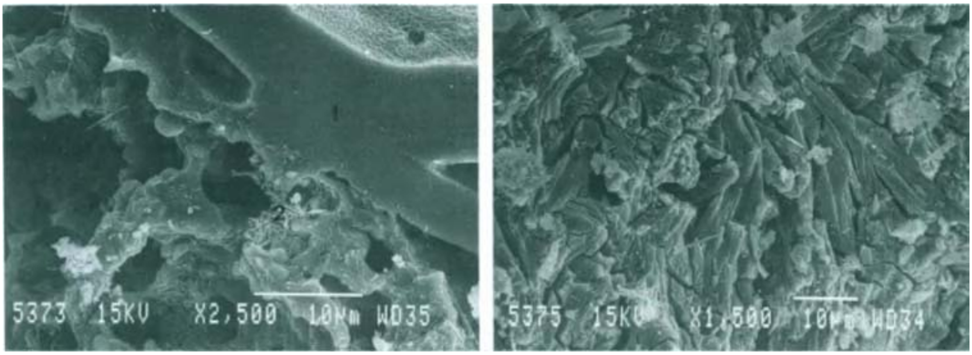
Table 3
Tests Los Angeles and Micro-Deval

	Fraction 5/20 mm
Los Angeles : L.A. (%)	42.6
Los Angeles (after frost-thaw cycles): L.A. (%)	44.8
Micro-Deval : MDE (%)	32.2
Frost sensitivity: G (%)	5.16

Table 4
Mineralogical analysis by XRD

Mineral	Fraction 0/5 mm	Fraction 5/20 mm
Quartz : SiO_2	+	+
Calcite : $CaCO_3$	++	+
Anhydrite :$CaSO_4$	+	t
Gehlenite :$Ca_2Al_2SiO_7$	+	+
Ettringite :$6CaO.Al_2O_3.3SO_3.31H_2O$	+	-
Glass	+++	+++

+++ very strong; ++ strong; + weak; t trace



1: vitreous, 2: ettringite   1: calcium sulfate

Fig. 2: Observation SEM of the MSWI bottom ash

C_2S particles associated with chlorine were also observed, as well as the particles of magnesoferrite, calcium chloroaluminate, calcium sulfate. The trace of metallic zinc and the presence of crystallized slag, gehlenite containing chlorine, carbonates, fly ash, glass and locally some asbestos fibers was also detected.

2.4. Chemical analysis

The chemical analysis of the MSWI bottom ash was realized on the fractions 0/2 mm, 0/5 mm and 5/20 mm in order to detect the possible variation of composition in different fractions. The results are reported in Table 5.

Among the major elements the SiO_2 content is higher in the coarse fractions than in the fine fractions, probably because of the higher content of glass in the coarse fractions. On the other hand, the presence of alumina, lime and sulfates in the fine fractions is higher than in the coarse fractions.

The inhibitor elements for the set of Portland cements such as Zn, Pb, P_2O_3S are rather concentrated in the finest fraction.

The alkali content in the MSWI bottom ash is very high, especially in the coarse fraction because of the glass. Therefore attention should be paid to the potential alkali-aggregate reaction.

The analysis of the total organic matter following the standard P94-055 is reported in Table 6 in % in weight. It can be found that the organic matter is also concentrated in the fine fraction.

3. TESTS ON MORTARS

The aptitude of the MSWI bottom ash to be used with hydraulic binders, particularly the setting time of the mixtures, was tested with an ordinary Portland cement CEM I 45,2 R and a slag cement CEM III 32,5 on mortars.

Table 5
Chemical analysis of different fractions of the MSWI bottom ash

Elements	Fraction 0/2 mm	Fraction 0/5 mm	Fraction 5/20 mm
	Major elements content (%)		
SiO_2	33.45	41.51	60.00
Al_2O_3	7.20	6.40	4.99
Fe_2O_3	6.83	7.43	7.29
CaO	23.02	20.08	13.99
MgO	2.58	2.66	1.59
SO_3	3.46	2.13	0.63
P_2O_5	1.66	1.36	0.50
Na^+	2.09	2.69	5.39
K^+	0.79	0.45	0.93
Cl^-	0.51	0.37	0.14
TiO_2	0.27	0.20	0.09
MnO	0.06	0.05	0.04
Cr_2O_3	0.04	0.05	0.05
SrO	0.07	0.06	0.05
Ig.	18.00	14.30	4.3
Total (%)	*100.03*	*99.74*	*99.98*
	Heavy metals content (ppm)		
Pb (ppm)	1172	1120	910
Zn (ppm)	5819	4660	2030
Cd (ppm)	72	60	50
Cr^{6+} (ppm)	10	20	20
As (ppm)	12	6	6
Hg (ppm)	348	< LD	< LD

LD: limit of detection

Table 6
Organic matter content in the MSWI bottom ash

Organic matter	Fraction 0/5 mm	Fraction 5/20 mm
(%)	1.92	0.99

Samples were prepared at the temperature 20°C and the relative humidity 71%±0.2, stored at 20°C and a relative humidity > 95% before demoulding and in water at 20°C after demoulding.

3.1. Setting time

According to the chemical analysis of different fractions of MSWI bottom ash, the tests on mortars were carried out first on the finest fraction 0/2 mm that is certainly the penalizing fraction in term of setting due to the high heavy metals content such as Zn, Pb and Portland cement setting inhibitors such as phosphates and organic matter.

Different treatments aiming to decrease or to eliminate the effect of the setting inhibitors by chemical reactions or by physico-chemical effects were conceived using the following secondary additions:

- quick lime
- extinct lime
- fly ash LFC type
- gypsum
- silica fume

A pre-immersion of MSWI bottom ash mixed with different additions for 4 hours was applied in order to further the expected beneficial effects taking place during the treatments.

The results reported in Table 7 were obtained on the reference mortars prepared only with the cement, ordinary Portland cement CEM I 42,5R or slag cement CEM III 32,5. These results show a generally very long setting time, especially with the finest fraction, confirming the higher inhibitor effect of the finest fraction.

The results obtained with different treatments are given in Table 8. The set of these mortars are generally faster than the reference mortars, especially for the treatment with silica fume which is more efficient.

Table 7

Setting time of the reference mortars using different fractions of MSWI bottom ash

(days)	Fraction	in water	to air
CEM I 42,5R	0.08/2 mm	12.0	5.0
	2/5 mm	2.0	1.5
	0/5 mm*	7.0	2.0
	0/5 mm* *	6.5	2.0
CEM III 32,5	0.08/2 mm	5.5	2.0

* without preimmersion in water, * * with preimmersion in water

Table 8

Setting time of the mortars with MSWI bottom ash 0/2mm by different treatments

Treatments	Cement	Additions and % to MSWI	Beginning - End (days)
T1	CEM III 32,5	10% CaO	3.3 - 3.9
T2	CEM I 42,5R	LFC	3.0 - 5.5
T3	CEM III 32,5	CAO + LFC	10.6 - 14.7
T4	CEM I 42,5R	20%LFC	1.2 - 1.7
T5	CEM I 42,5R	10%$Ca(OH)_2$+10%gypse	0.8 - 1.1
T6	CEM I 42,5R	20%FS	0.2 - 0.9
T7	CEM I 42,5R	10%FS	1.4 - 3.6
T8	CEM III 32,5	9%FS+1%$Ca(OH)_2$	5.0 - 5.9

3.2. Mechanical strength

Samples were prepared with different fractions of MSWI bottom ash and EN standardized sand according to the following composition:

- for EN sand, the composition of the mortar is that described in the standard EN 196-1,
- for different fractions of MSWI, the binder to MSWI bottom ash ratio is the same as with EN sand, but the water to binder ratio is adjusted to obtain the same consistency as with EN sand,

The setting time of the tested mortars being very long, it is impossible to measure the flexural, compressive strength and the elastic module at the initial ages. The storage in air at 20°C allowed nevertheless a setting. The results are illustrated in Figure 3.

3.3. Shrinkage and expansion in water

The shrinkage and the expansion in water were measured following the standard NF P 15-433 on samples 4x4x16 cm (Figures 4 and 5).

It can be observed from these results that the shrinkage is higher with ordinary Portland cement CEM I and particularly for the fraction 0/5 mm, while the expansion is stronger with slag cement CEM III for the fraction 2/5 mm.

3.4. Alkali-aggregate reactivity

A test of alkali-aggregate reactivity was made following the standard NF P 18-585 on samples 2x2x28 cm placed in a reactor saturated in humidity and at 38°C, an ordinary Portland cement CEM I 42,5R and MSWI bottom ash 0.16/5 mm being used.

Instead of the expansion, a phenomenon of shrinkage is recorded. Nevertheless, the interpretation of this result should be given with caution taking into account the particular preparation conditions related to the rheology of the mortars and the very high porosity of the samples which may mask the possible expansion. Examinations under the scanning electronic microscope (SEM) show in fact a very high porosity with a lot of air bubbles in the matrix and the frequent presence of ettringite, but the products alkali-aggregate reaction in relation with the alkalis in the MSWI bottom ash were not detected.

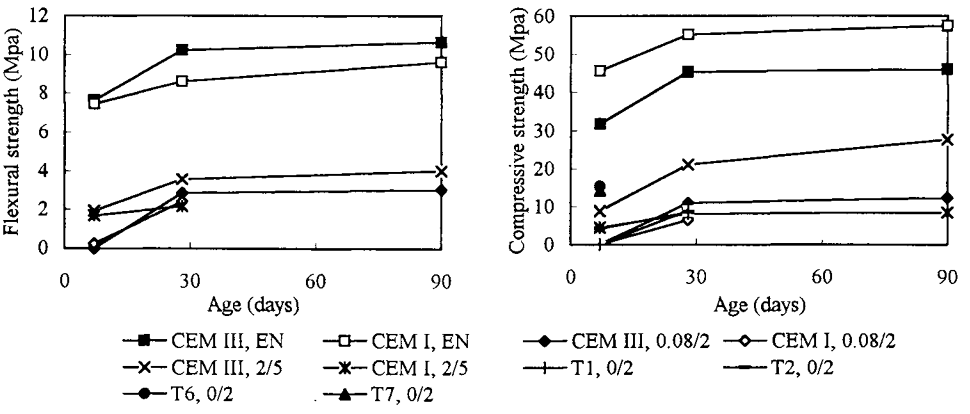


Fig. 3: Flexural and compressive strength of the mortars

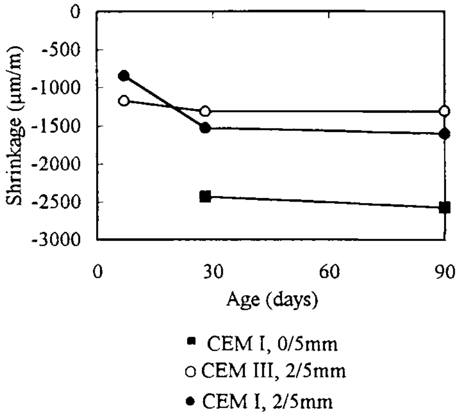


Fig 4: Shrinkage of the mortars

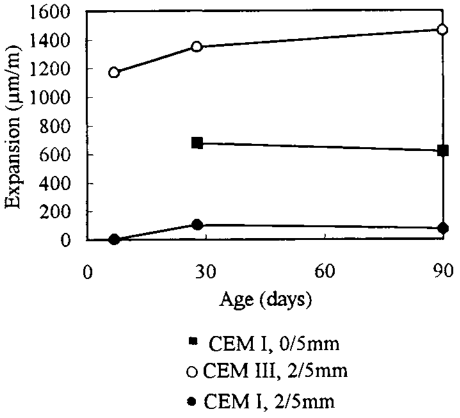


Fig 5: Expansion of the mortars

3.5. Leaching

A leaching test on mortars without treatment was carried out following the standard NF X31-210, in order to measure the heavy metals non fixed by the cement matrix.

Table 9
Leaching test on mortars

Fraction	0/5 mm		2/5 mm
Cement	CLK CEM III	CPA CEM I	CPA CEM I
Pb (ppm)	< LD	15	10
Zn (ppm)	< 1	< 1	< 1
Cd (ppm)	< LD	< 1	< 1
Cr^{6+} (ppm)	< 1	< 1	< 1
As (ppm)	< 1	< 1	< 1
Hg (ppm)	< LD	< LD	< LD

LD: limit of detection

From theses results (Table 9), it can be observed that the heavy metals brought by the MSWI bottom ash are nearly completely stabilized in the matrix of cement. However the Pb is still detected in the state of trace.

3.6. Conclusions on mortars

The tests on mortars allow to clear the following essential points:

- the set of mortars based on CPA/CEM I or CLK/CEM III and MSWI bottom ash is very slow and it is slower with an increased proportion of MSWI bottom ash;
- the mechanical characteristics such as flexural, compressive strength and elastic module are weak, they are impossible to measure at the initial ages;
- the shrinkage and the expansion are relatively stronger compared to mortars without MSWI bottom ash;

- the alkali-aggregate reactivity of the MSWI bottom ash is not observed on the tested mortars;
- the matrix of cement has a interesting capacity to stabilize heavy metals. However, the Pb is still present in the state of trace;
- among the different treatments, the addition of silica fume to the mixture composed of the MSWI bottom ash and the hydraulic binder type CPA/CEM I or CLK/CEM III allows a relatively fast set, with interesting mechanical characteristics.

4. TESTS ON CONCRETES

To complete the tests on mortars, tests on concretes were programmed using the secondary additions such as silica fume, silico- alumineous fly ash, natural pozzolan and diatomaceous powder. The main characteristics concerned are the setting time, the mechanical strength, the shrinkage and expansion. These tests are completed by the microstructural examination under scanning electronic microscope.

4.1. Concretes with silica fume

Based on some preliminary tests, the following formulations were studied :

• cement and content:	CLK CEM III 32,5, 400 kg/m^3 or CPA CEM I 52,5 R, 325 kg/m^3
• addition:	silica fume, 30 to 150 kg/m^3
• W/C ratio:	0,47 to 0,88 to obtain constant workability
• aggregates:	(a) 100% MSWI - 0/5 mm as sand + 5/20 mm as coarse aggregate (b) natural sand + MSWI 5/20 mm as coarse aggregate (c) natural sand+(50%MSWI5/20mm+50%natural coarse aggregate) (d) natural sand + natural coarse aggregate
• admixture:	superplasticizer Cimfluid 2000 AC

4.1.1. Mechanical strength

The results are illustrated in Figure 6. All concretes gave a characteristic strength at 28 days higher than 20 MPa or even 25 MPa.

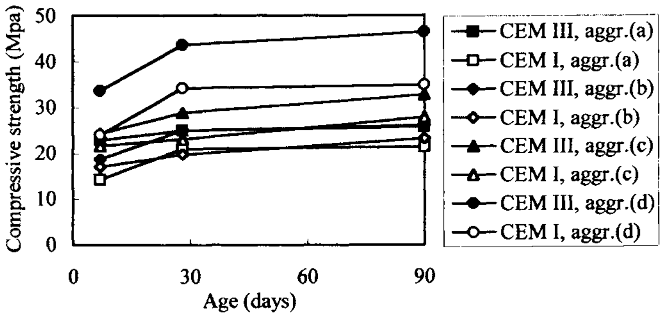


Fig. 6: Compressive strength of the concretes

4.1.2. Shrinkage and expansion

The shrinkage in air and the expansion in water of the concretes were measured. The results are illustrated in Figure 7.

It is observed from these results that the most important expansion and the highest shrinkage in a least measure were recorded for formulations based on CLK CEM I cement and with 100% MSWI. The absolute value of the shrinkage and the expansion is comparable to this of a normal concrete or even lower.

4.1.3. Leaching

The leaching tests were carried out according to the standard NF X31-210 on concretes prepared with 100% MSWI bottom ash and based on CPA CEM I cement and CLK CEM III cement. The results are given in Table 10.

These results show that Pb and the Hg can be still leached, but only in the state of a trace.

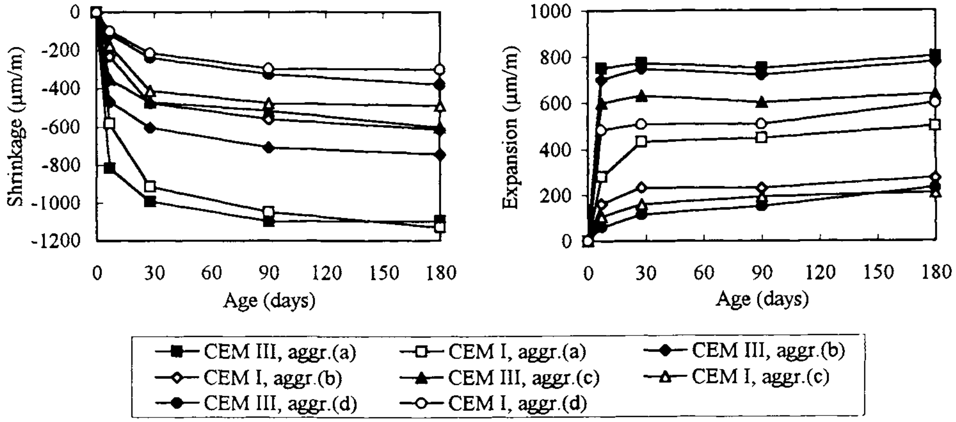


Fig. 7: Shrinkage and expansion in water of the concretes

Table 10

Leaching test on concretes with 100% MSWI bottom ash

(ppm)	CLK CEM III	CPA CEM I
Zn	< 1	< 1
Pb	< 2	< 2
Hg	< 2	< 2
Cd	< 1	< 1
Cr^{6+}	0,1	0,4

4.1.4. Microstructural examination

Observations under scanning electronic microscope (Figure 8) show a very high porosity and microporosity in the matrix, in relation with many spherical air bubbles.

The bond between the cement matrix and the particles of MSWI bottom ash, especially with the glass, are generally very weak and even non-existing.

The ettringite crystals are very well formed around or even inside the porous particles of MSWI bottom ash grains, as well as in certain porous zones of the cement matrix. The aluminum was sometimes observed. The silica fume particles could be rarely recognized.

4.2. Concretes with fly ash

The goal of this new phase aims the feasibility of concretes using MSWI bottom ash as aggregates and more economic and available fly ash as addition instead of silica fume which is efficient but expensive for the valorization of the MSWI bottom ash in concretes.

4.2.1. Formulations and treatments

The formulations and the different treatments are indicated in Table 11. These formulations use a silico-alumineous type fly ash in combination with lime and gypsum. The treatments are based on the tests of setting time carried out beforehand on mortars, a reduced setting time being the first characteristic to be reached.

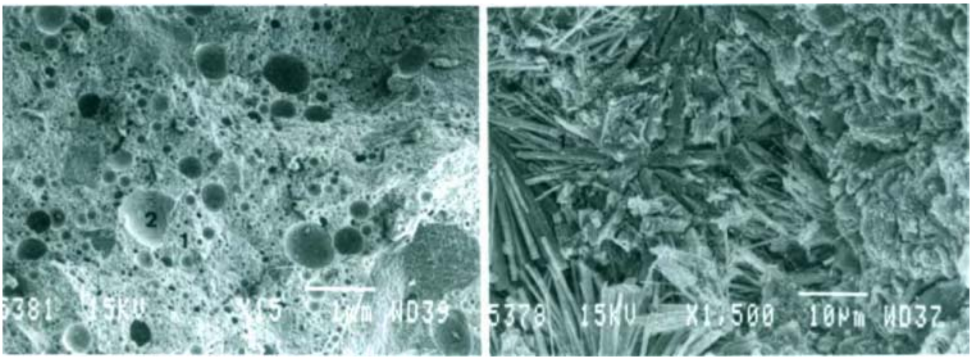
The following treatments were applied:

Treatment A: Immediate global mixing of all ingredients of concrete

Treatment B: Initial mixing of all ingredients of concrete except cement and admixture, followed by a rest period of 4 hours and finished by the global mixing with the cement and the admixture

Treatment C: Initial mixing of all ingredients of concrete except cement, fly ash and admixture, followed by a rest period of 4 hours and finished by the global mixing with the cement, fly ash and the admixture

The quantity of admixture was approximately adjusted in order to get a concrete with an expected consistency.



1: cement matrix, 2: air bubbles

1: ettringite formed around MSWI particles

Fig. 8: Microstructure of the concretes

Table 11
Formulations and treatments for the concretes

	General formulation (kg/m^3)	
Cement:	CPA CEM I 52,5R	300
	silico-alumineous fly ash	114
Addition:	extinct lime	47.6
	gypsum	13.6
Water:		240
MSWI:	0/2.5 mm as sand	429
	5/20 mm as coarse aggregate	841
Admixture:	Cimfluid AC (l/m^3)	3.7 to 6.9

	Concretes and treatments	
Concrete N°	Additions used	Treatment
1	fly ash	A
2	fly ash, lime	A
3	fly ash, lime, gypsum	A
4	fly ash, lime	B
5	fly ash, lime, gypsum	B
6	fly ash, lime	C
7	fly ash, lime, gypsum	C

4.2.2. Results

The following characteristics were determined : the slump of the fresh concretes, the mechanical strength and the expansion in water.

The results show that the workability of the fresh concretes can be easily reached by adjusting the quantity of superplasticizer in normal range. All concretes were prepared to obtain a plastic or very plastic consistency. This will allow to decrease further the water to binder ratio and therefore to increase the initial strength and the long-term strength.

All concretes underwent the setting and gave a strength at 1 day although it remains still low. The optimization of the formulation, especially the reduced water to binder ratio will improve the mechanical characteristics.

Comparing the strength at 1 day and at 7 days (Table 12), the difference between the treatments for a same formulation and between the formulations for a same treatment remains relatively small and random. A specific treatment process doesn't seem necessary. In this sense, the use of fly ash in substitution of silica fume constitutes an advantageous solution because of the simplicity of concreting.

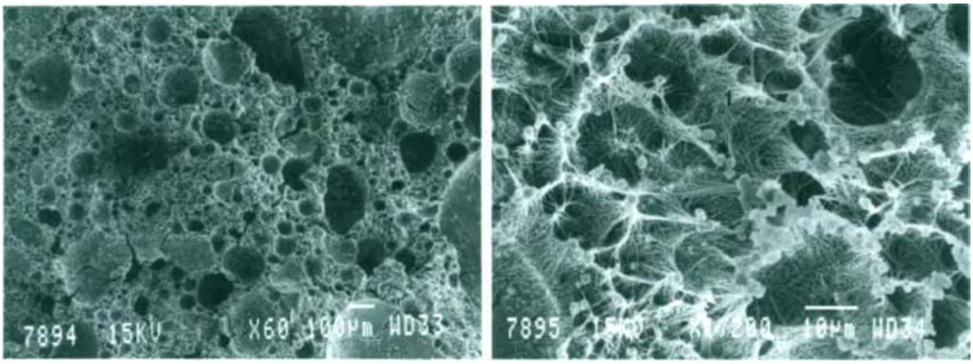
However, cracks probably induced by the internal expansion appeared in the samples after four weeks of storage in water and the mechanical strength at 28 days was impossible to be measured.

An examination of the cracked samples under the scanning electronic microscope showed that these cracks are related to the massive crystallization of ettringite (Figure 9). The ettringite formation must be caused by the reaction of anhydrite present in MSWI bottom ash with the added lime and the alumina compound present in the cement and the fly ash.

Table 12

Compressive strength of the hardened concretes (MPa)

Concrete N°	1	2	3	4	5	6	7
at 1 day	3.1	5.5	4.2	6.7	6.7	3.8	8.0
at 7 days	8.8	13.5	10.8	11.9	10.8	7.5	14.6



1: cement matrix, 2: air bubbles

1: ettringite formed in air bubbles and in the matrix

Fig. 9: Microstructure of the cracked samples (SEM)

4.3. Concretes with a pouzzolan cement and a diatomaceous powder

Tests on concretes with a pouzzolan cement CPZ CEM IV/B 32,5 and a diatomaceous powder were also undertaken. The formulations are given in Table 13. The quantity of admixture was approximately adjusted to obtain a plastic or very plastic concrete. For the concrete with diatomaceous powder, a supplementary quantity of water was added due to the high absorption capacity of the very fine diatomaceous powder (specific surface 680 m^2/kg).

Taking into account the results of the concretes with fly ash, no treatment was applied for the concretes with the pouzzolan cement and the diatomaceous powder.

The fresh concretes with diatomaceous powder underwent a bit slower set than the concretes with silica fume and fly ash, but less than 24 hours. The fresh concretes with CPZ CEM IV/B cement, especially CPZ1, underwent a slower set more than 24 hours (but less 36 hours). The measurement of the strength at 1 day was impossible.

Table 13

Formulations of the concretes

kg/m^3	CPZ1	CPZ2	Diatom.
Cement	CPZ CEM IV/B, 414	CPZ CEM IV/B, 414	CPA CEM I 52,5R, 300
Addition	-	-	diatom. powder, 114
Water	240	240	263
Fine aggr.	MSWI 0/5mm, 429	MSWI 0.1/5mm, 429	MSWI 0/5mm, 429
Coarse aggr.	MSWI 5/20mm, 841	MSWI 5/20mm, 841	MSWI 5/20mm, 841
Admixture	Cimfluid 2000, 6.5 l/m^3	Cimfluid 2000, 6.5 l/m^3	Cimfluid 2000, 9.5 l/m^3

Generally, the compressive strength at 7 days and at 28 days is relatively low because of the high water to cement ratio, but it still increases at 60 days (Figure 10).

Giving the same formulation used for two concretes CPZ1 with MSWI 0/5 mm as sand and CPZ2 with MSWI 0.1/5 mm as sand, the difference of strength between two concretes indicates the high effect of the finest fraction 0/0.1 mm of the MSWI bottom ash on mechanical properties of concrete.

No great expansion was observed up to more than two months (Figure 11). The results should be interpreted with caution and the measurement of the length change will continue.

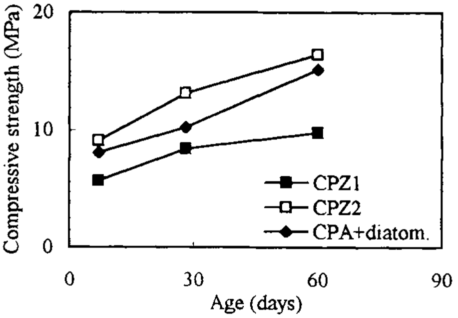


Fig. 10: Compressive strength of the concretes

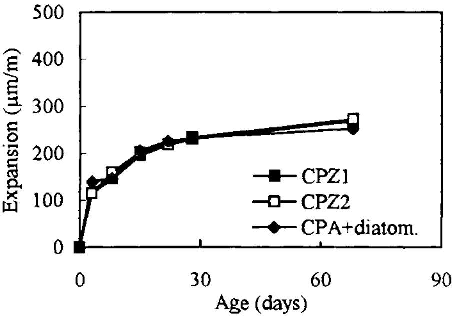


Fig. 11: Expansion of the concretes

5. CONCLUSIONS

The valorization of MSWI bottom ash as aggregate in concrete is aimed in the present work. Based on various formulations and treatments, the tests on mortars and concretes using MSWI bottom ash as aggregate were carried out in order to get different interesting technical solutions.

The MSWI bottom ash contains a high quantity of setting inhibitors for Portland cement. The different treatments used in this work showed that the mortars with silica fume as addition underwent a almost normal set and a high enough mechanical strength, and the concretes prepared with these formulations correspond to a concrete B20 or B25. The effect given by silica fume may be related to the physical absorption of the heavy metals and inhibitor elements and the chemical pouzzolanic reaction in mortars and concretes. However, from the economic point of view, the relatively high cost of silica fume which is used with non negligible proportions penalizes the financial profitability for the valorization of the MSWI bottom ash.

The tests on concretes with fly ash as addition also underwent a relatively fast set and a good enough initial strength. Moreover, a specific treatment process doesn't seem necessary. However, after four weeks of storage in water, some cracks appeared. These cracks are caused by the massive ettringite formation which may come from the reaction between the added lime, the calcium sulfate and the alumina compound from the fly ash and the MSWI bottom ash. In this sense, particular attention should be paid when lime and fly ash are used in the treatment of MSWI bottom ash.

The concretes prepared with a pouzzolan cement and a diatomaceous powder gave a bit longer set and the mechanical strength is relatively low because of the high water to cement ratio. No great expansion was observed up to the writing of this paper (more than two months).

All concretes tested in this work have a good workability which allows to decrease further the water to binder ratio and therefore to increase the mechanical strength and to improve the durability. Systematic microstructural studies showed that the matrix of these concretes is very porous due to the high presence of spherical air bubbles. The further study should take into account the air-entraining effect of the MSWI bottom ash in concrete in order to get higher mechanical characteristics.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Life-cycle impacts of the use of industrial by-products in road and earth construction

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A two-stage study "Life cycle analysis of road construction and earthworks" was part of a more extensive Finnish research project "Assessment of the applicability of secondary products in earthworks". In the first stage of this work a life-cycle impact assessment procedure for the comparison and evaluation of alternative road and earth constructions was developed. Additionally, a database containing the environmental burdens of the most significant construction materials and unit operations was constructed. In order to evaluate the applicability of the procedure, the use of coal ash, crushed concrete waste and granulated blast-furnace slag in road construction was evaluated in case studies. The use of these secondary products was also compared with the use of natural materials in corresponding applications.

The aim of the second stage was to transfer the assembled data for utilisation as a practical model by creating an inventory analysis program to calculate and compare the life cycle impacts of the most common road constructions and foundation engineering methods. The data obtained in the first stage was also augmented to the extent necessary for this purpose.

The results of case studies indicate that the production and transport of the materials used in road constructions produce the most significant environmental burdens. Production of the bitumen and cement, crushing of materials and transport of materials are the most energy consuming single life-cycle stages of the construction. A large part of the emissions to atmosphere originates from energy production. In the expert assessment, consumption of natural materials and leaching behaviour were also regarded being of great significance.

1. BACKGROUND

About 70 million tonnes of natural mineral aggregates are used each year in Finland for road construction and earthworks. Depletion of the best materials, the need for resource conservation and lengthened transport distances have all increased the need to introduce substitute materials for natural aggregates. At the same time industry, construction and other similar activities produce large quantities of secondary products, which may be suitable for use.

Up to now mainly coal fly ash and bottom ash, blast furnace slag and crushed concrete have been used in Finland. Also asphalt pavements are being recycled into materials for new pavements. Shredded tyres, steel and metal industry slags and foundry sand are used in smaller amounts, and on-going research and test projects are seeking to improve the prerequisites for usage of these and several other materials.

One of the barriers to the wide-ranging utilisation of the secondary products of energy production and industry in road construction has been uncertainty about the environmental impacts. In order to prevent potentially hazardous effects it is important to identify all the positive and negative impacts of these materials. Life cycle impacts are also being increasingly used as a selection criterion for products and materials both in industry and in other activities.

Describing the total environmental impacts of activities and products reliably and in such a way that alternatives can be compared is no simple task. The cradle-to-grave life cycle analysis involves numerous stages and activities that give rise to different environmental loadings. Identification of the critical stages of the life cycle and those factors responsible for environmental loadings requires not only adherence to the basic principles of life-cycle-analysis but also knowledge of the product or activity in question.

The special characteristics of road construction and earthworks are large volumes of the materials consumed, the long service lives of the finished products, the need to assess construction as a whole rather than comparing alternative materials, and the significant effect of the construction's longevity and need for repair on their life cycle environmental loadings.

2. DEVELOPMENT OF LCA-METHODOLOGY

A life-cycle impact assessment procedure for the comparison and evaluation of alternative road and earth constructions was developed (Mroueh et al. 2000). The procedure focused especially on the comparison of industrial by-products and natural aggregates, but the assessment of other constructions is possible, as well. The following basic requirements were set for the methodology: the method must be straightforward and easy to use, but at same time all major unit processes and environmental impacts must be included. In addition, particular attention should be paid to the special characteristics of earth construction. One premise was also that the assessment procedure should be applicable as a part of road planning, and that the results could be used as selection criteria for alternative constructions and materials.

The analysis included all the significant life-cycle stages covering the production and transportation of materials, their placement in the road structures and the use of the construction. The situation after the use of the construction was not included because the structures most commonly remain in place after they have been withdrawn from service.

Those stages of road construction and use that have no significance for the comparison of constructions were ruled out from analysis for the moment. These included:

- site clearance
- functions associated with road use, e.g. lane markings, the installation and use of lights and traffic signs
- regular and seasonal maintenance, such as snowploughing, road salting and sanding
- traffic emissions, which are significant in comparisons only if it is possible to determine the effect of using a material or structure on them.

In the comparisons, the functional units were always structures of the same dimensions that met the same performance requirements and were designed at the same site. The road constructions were studied as entities. Because the environmental loading data was calculated for each individual structural component and work stage, it was also used for examination of selected courses or work stages. 50 years was chosen as the period of analysis. The period must be sufficiently long to include the impacts of road service life.

The foundation and pavement structures were analysed separately and combined if required. In the case of industrial by-products the environmental burdens of the landfill disposal were also assessed, as an alternative to their use in road construction.

The environmental burdens dealt with were limited to those assessed as being the most important for road construction in expert assessment. The following environmental loadings were included in the inventory:

1. Use of resources	Natural materials Industrial by-products Energy and fuel consumption
2. Atmospheric emissions	Carbon dioxide (CO_2) Nitrogen oxides (NO_x) Sulphur dioxide (SO_2) Volatile organic compounds (VOC) Particles Carbon monoxide (CO)
3. Leaching into the ground	Heavy metals Chloride Sulphate
4. Other loadings	Noise Dust Land use

On the basis of a preliminary assessment of the quantity and significance, the following environmental loadings were excluded from the inventory: water use, discharges of COD and nitrogen to water, emissions of PAH, heavy metals and methane, ordinary and hazardous waste and accident risks.

3. CASE STUDIES

3.1 Pavement structures

The use of conventional materials and secondary products was compared in a pavement structure which was designed according to the design code of the Finnish Road Association (STS 29). The dimensions of the structure are presented in Figure 1.

The life cycle environmental loadings were calculated for the alternative constructions listed in Table 1. Because the same structural requirements can be met using different structural solutions, two different alternatives in terms of pavement thickness were designed for the fly ash and crushed concrete constructions. In addition, a fly ash construction in which cement was not used as a mix additive was inventoried. With the aid of alternative by-product constructions it was possible to assess the effects of the pavement course thickness and the use of cement on the life cycle environmental loadings.

Table 1. Structural courses of the case study constructions and the materials used in them. The constructions and the abbreviations hereafter used to denote them were as follows:

Natural aggregate - reference construction built solely out of natural mineral aggregate, R1
Ash 1 - fly ash construction, FA1
Ash2 - fly ash construction comparable with other constructions in terms of pavement thickness, FA2
Ash3 - fly ash construction 2 without cement, FA3
Concrete1 - crushed concrete construction, CC1
Concrete2 - crushed concrete construction in which the pavement thickness is reduced by using thicker crushed concrete courses than in Concrete 1, CC2
Blast-furnace slag - construction in which crushed blast-furnace slag and sand are used, BFS.

Structural layer	**Natural aggregate**	**Ash1**	**Ash2**	**Ash3**	**Concrete1**	**Concrete2**	**Blast-furnace slag**
Pavement	160 mm AB 20/120	50 mm AB 16	160 mm AB 20/120	160 mm AB 20/120	160 mm AB 20/120	80 mm AB 20/120	160 mm AB 20/120
Base course	250 mm Crushed stone 0-35	150 mm Crushed stone 0-35 BST	150 mm Crushed stone 0-35	150 mm Crushed stone 0-35	100 mm Crushed concrete 0-50	200 mm Crushed concrete 0-50	100 mm Crushed blast-furnace slag
Sub-base	250 mm Gravel	650 mm Fly ash + cement 2%	350 mm Fly ash + cement 2%	350 mm Fly ash	350 mm Crushed concrete	200 mm Crushed concrete	250 mm Granulated blast-furnace slag
Filter layer	250 mm Sand	200 mm Sand	200 mm Sand	200 mm Sand	550 mm Sand	450 mm Sand	200 mm Granulated blast-furnace slag
Total thickness	**960**	**1050**	**860**	**860**	**960**	**930**	**860**
Embankment	500 mm Sand	500 mm Sand	500 mm Sand	500 mm Sand	500 mm Sand	500 mm Sand	500 mm Sand

The functional unit selected for the case studies was a one-kilometre-long section of road, the structural design of which is given in Figure 1. Average distances from the Helsinki Metropolitan Area to sources of sand, gravel, crushed rock and fly ash were used as the transport distances.

Average transport distances in Finland were used for other raw materials. The transport distances were as follows:

Crushed rock	10 km	Crushed concrete	10 km
Sand and gravel	50 km	Cement	100 km
Fly ash	10 km	Asphalt	10 km
Blast-furnace slag	50 km		

In these theoretical cases it was not possible to determine the effect of the structural materials on road maintenance. Thus the calculations were limited to only one maintenance alternative, which describes the contribution of road maintenance to the total life cycle loadings of the construction.

The consumption of natural materials and the by-product quantities in the alternative pavement structures are given in Figure 2. In the by-product constructions the consumption of natural materials is primarily influenced by the extent to which different materials of the structural courses can be replaced by secondary materials. The differences between the alternative constructions are reduced by the fact that a 0.5-metre sand embankment and asphalt pavement is assumed in all the constructions.

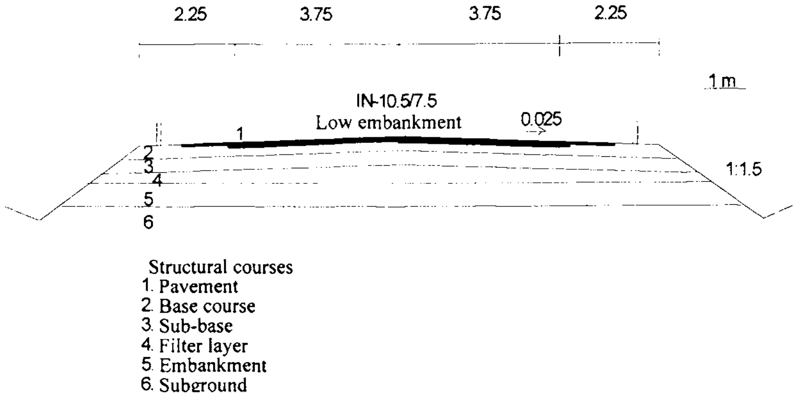

Figure 1. Dimensions of the cross-section selected for analysis and the structural courses on a low embankment.

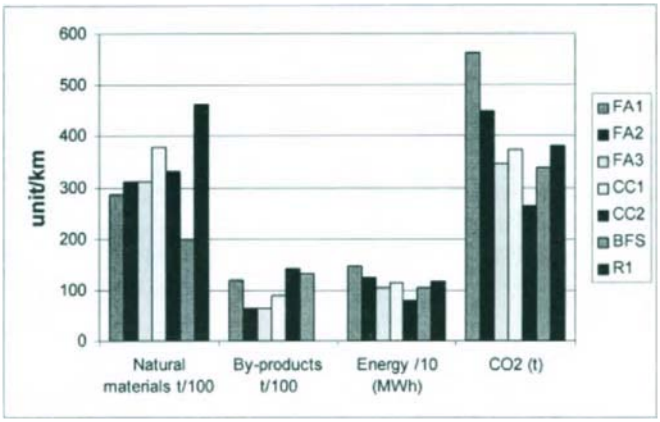

Figure 2. Comparison of material and energy use and emissions of CO_2 of the alternative pavement studies. FA1, FA2 and FA3 – fly ash constructions; CC1 and CC2 – crushed concrete constructions; BFS – blast furnace slag construction, R1 – natural aggregate construction.

The energy consumption of the alternative constructions by main work stage is presented in Figure 3. Most of the energy is consumed in the pre-handling phase, which includes the heavily energy-consuming manufacture of cement and asphalt. In the fly ash construction FA1, for example, asphalt accounts for 57% of energy consumption, the manufacture of cement for 25%, and everything else for only 18%. The fly ash constructions containing

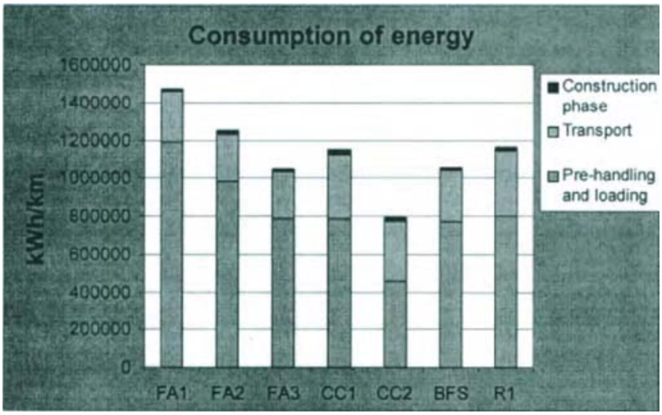

Figure 3. Consumption of energy of the alternative pavement structures. FA1, FA2 and FA3 – fly ash constructions; CC1 and CC2 – crushed concrete constructions; BFS – blast furnace slag construction, R1 – natural aggregate construction.

cement (FA 1 and 2) have the highest total energy consumption, and the crushed concrete construction with a relatively thin asphalt pavement (CC2) has the lowest. The share of transport is 15 – 30 % of energy consumption.

With the exception of some process emissions, the atmospheric emissions originated from the consumption of fuels, and they were broken down among the alternative constructions, structural materials and work stages in the same way as energy consumption.

Some environmental loadings of the alternative pavement structures are compared in Figure 2. For comparison, Table 2 also shows the traffic emissions over a period of 50 years, assuming a traffic volume of 7,000 vehicles per day, of which 1,000 are heavy vehicles.

The tables and figures clearly show that there are differences between the environmental loadings of the pavement structures in the case studies. Because the constructions were examined as a whole, the use of asphalt accounts for a relatively large proportion of energy consumption and atmospheric emissions. This evens out the differences between the constructions with regard to these loadings. The same type of levelling effect is also evident in the other loadings.

Table 2. Energy consumption and atmospheric emissions of the construction of alternative pavement structures compared to the traffic emissions over a period of 50 years (Häkkinen & Mäkelä 1996, Puranen 1992, Pirilä et al. 1997, Mäkelä et al. 1996).

Effect category	**Unit**	**FA1**	**FA2**	**FA3**	**CC1**	**CC2**	**BFS**	**R1**	**Traffic**
Energy consumption	MWh/km	1 470	1 250	1 050	1 150	793	1 060	1 160	120 200
Emissions									
-CO	kg/km	1 120	900	650	800	760	600	830	459 000
-NO_x	kg/km	3 800	3 400	2 900	3 300	2 600	2 800	3440	354 000
-particles	kg/km	360	310	260	300	250	260	315	22 000
-SO_2	kg/km	610	530	440	450	280	425	460	4 000
-CO_2	t/km	562	449	346	373	263	338	380	31 500
-VOC	kg/km	980	870	740	790	550	720	800	86 000
-dust (2–40 μm)	kg/km	3 020	8 540	8 540	4 200	3 800	3 100	14 000	

In these case studies the use of blast-furnace slag and crushed concrete reduced the environmental loadings compared to the use of natural aggregates. When comparing the environmental loadings, it must, however, be remembered that we were dealing with theoretical constructions. In real situations the calculation must always be made for each individual construction. For example, a change in the thickness of the asphalt course, the use of unpaved structures or the use of cement has a significant effect on the total loadings and also on the differences between the constructions. The difference between the FA2 and FA3 fly ash constructions illustrates the effect of using a relatively small amount of concrete (2 % of the material used in a 350 mm thick sub-base) on energy consumption and emissions.

3.2. Environmental loadings of the foundation engineering methods

In the alternative foundations examined, the natural ground was assumed to be weakly bearing and compressible soft clay extending to a depth of 5 metres. The ground beneath the clay was bearing. Constructions most commonly used on shallow and deep layers of weak soil were examined as alternatives. To make comparisons easier, the depth of weak soil was assumed to be the same in all the constructions. The alternatives were as follows:

Shallow layer of weak soil:	Soil replacement	Removal of the weakly bearing material and replacement by sufficiently bearing fill.
	Soil stabilisation	Stabilisation of the clay layer using cement (100 kg/m^3)
Deep layer of weak soil:	Deep stabilisation	Deep stabilisation using cement (120 kg/m^3) and a copping layer of stabilised clay
	Vertical drainage	Vertical strip drains at 1-metre intervals

A summary of the environmental loadings of the alternative foundation engineering methods is presented in Figure 4. Energy consumption and atmospheric emissions are high in the soil stabilisation and deep stabilisation alternatives, in which plenty of cement is used. Compared with the alternative pavement structures, the energy consumption of soil stabilisation and deep stabilisation are greater by factors of about 10 and 4, respectively.

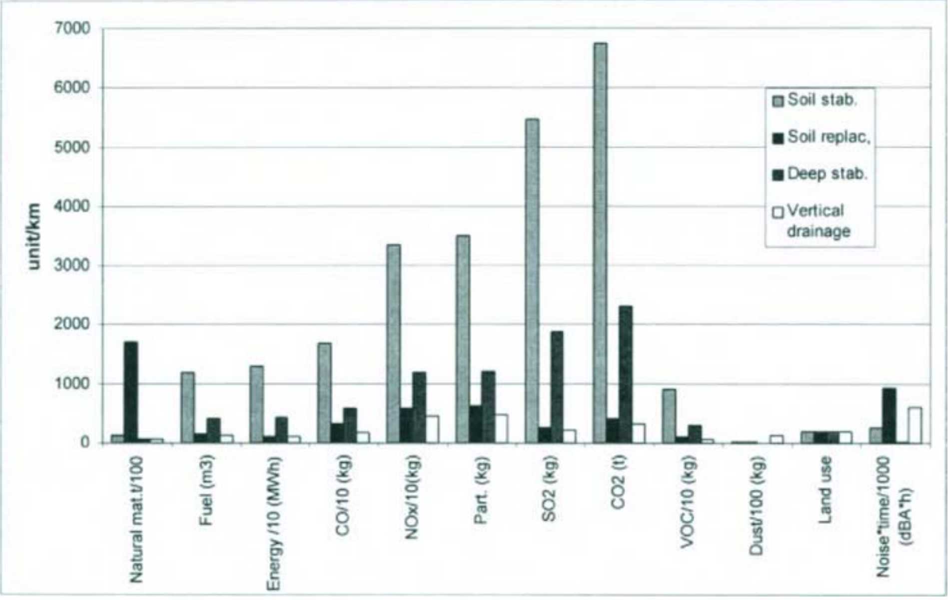

Figure 4. Environmental loadings of the alternative foundation engineering methods.

4. DATA DEFICIENCIES AND UNCERTAINTIES

Because of the local nature of the effects of road constructions, primarily local or material-specific data was used. Use was also made of general Finnish knowledge, which was supplemented by international sources of data where necessary.

Average Finnish leaching data was used for industrial by-products. Because there was no leaching data for natural aggregates, a few materials were tested during the project. The tests used were CEN pr EN 12457 (L/S 2 and L/S 10) and a pH-static test. In CEN pr EN 12457 the leaching of Cd, Cr, Zn and Pb and V were under detection limit (Table 3) from all the natural aggregates. The decrease of pH did not significantly increase the leaching of metals from sand. The amounts of Cu, Ni and Zn leaching from crushed rock and crushed gravel increased in the pH-static test.

The quantities of substances leaching out of secondary materials were simulated on the basis of laboratory-scale leaching tests. In practice, numerous factors, e.g. the condition of the structure and its surface as well as environmental conditions, affect leaching from construction materials.

The availability of data on by-products was limited by the fact that their utilisation is not yet well established. For this reason it is not always easy to determine the most common working methods and the most general implementation methods of the work stages. As yet there is still relatively little experience- or measurement-based data on the work stages and their environmental loadings.

The release of dust emissions from materials during the different stages of production, transportation and construction is a significant environmental loading factor due to the comfort and heath risks that they pose. However, little measurement data on the release of dust emissions was found and its conversion into a comparable form was problematic. In practice, small particulate matter (SPM) can be more significant than the total amount of particles. SPM emissions remain airborne for a very long time and are carried long distances by winds. Moreover, they pose a more serious health risk than bigger dust particles. Because SPM emissions have attracted attention only recently, there is even less data available on them than on total emissions of particles.

5. CONCLUSIONS

An Excel-based life cycle inventory analysis program for road constructions has been developed on the basis of the study's results. It covers all the work stages from material production to road maintenance as well as the materials most commonly used in the structural courses of road constructions. The environmental loadings of the constructions and structural components made from the materials within the scope of the program can be calculated simply using only the dimensions of the construction and thickness of the structural courses as input data. The inventory analysis program is limited at this stage to calculating and comparing the environmental loadings of constructions only.

Table 3. Leaching of metals from natural aggregates, mg/kg. Test method CEN prEN 12457.

Sample	**mg/kg**																	
	Cd		**Cr**		**Mn**		**V**		**Ni**		**Pb**		**Zn**		**As**		**Mo**	
	L/S 2	**L/S 10**	**L/S 2**	**L/S 10**	**L/S 2**	**L/S 10**	**L/S 2**	**L/S 10**	**L/S 2**	**L/S 10**	**L/S 2**	**L/S 10**	**L/S 2**	**L/S 10**	**L/S 2**	**L/S 10**	**L/S 2**	**L/S 10**
Crushed rock 0-50 mm	0,0002	0,001	0,004	0,020	**0,026**	**0,130**	0,010	0,050	0,004	0,020	0,004	0,020	0,040	0,200	**0,006**	0,030	0,020	0,1
Crushed rock 0-16 mm	0,0002	0,001	0,004	0,020	**0,006**	**0,046**	0,010	0,050	0,004	0,020	0,004	0,020	0,040	0,200	**0,006**	**0,030**	**0,024**	0,1
Filter layer sand	0,0002	0,001	0,004	0,020	**0,036**	**0,114**	0,010	0,050	0,004	0,020	0,004	0,020	0,040	0,200	0,006	0,030	0,020	0,1
Gravel	0,0002	0,001	0,004	0,020	**0,i28**	**0,338**	0,010	0,050	0,004	0,020	0,004	0,020	0,040	0,200	0,006	0,030	0,020	0,1
Gravel	0,0002	0,001	0,004	0,020	**0,072**	**0,368**	0,010	0,050	**0,004**	0,020	0,004	0,020	0,040	0,200	0,006	0,030	0,020	0,1
Crushed rock 0-16 mm	0,0002	0,001	0,004	0,020	**0,018**	**0,082**	0,010	0,050	0,004	0,020	0,004	0,020	0,040	0,200	0,006	0,030	**0,028**	0,1
Crushed gravel 0-50 mm	0,0002	0,001	0,004	0,020	**0,120**	**0,395**	0,010	0,050	0,004	0,020	0,004	0,020	0,040	0,200	0,006	0,030	**0,028**	0,1
Granulated blast furnace slag	0,0002	0,001	0,004	0,020	**0,211**	**0,301**	**0,403**	**1,753**	0,004	0,020	0,004	0,020	0,040	0,200	0,006	0,030	0,020	0,1

	Detection limit, mg/kg																	
	0,0002	0,001	0,004	0,02	0,002	0,01	0,01	0,05	0,004	0,02	0,004	0,02	0,04	0,2	0,006	0,03	0,02	0,1

The environmental loadings dealt with in the program have been limited to those assessed as being the most important. However, the loading factors in question described the total environmental loadings quite well as long as the life cycle inventory pertains to complete constructions. The environmental loadings regarded as being the most important for road construction in the expert assessment made when creating the inventory analysis procedure were the use of natural materials, energy and fuel consumption, the leaching of heavy metals into the soil, and atmospheric emissions of NO_x and CO_2.

In the case study it was found that the use of blast-furnace slag and crushed concrete decreased the environmental loadings compared to the reference construction. Because the construction and the transport distances always affect the outcome of such comparisons, the results as such cannot; however, be generally applied to the comparison of materials.

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Assessment of environmental impacts of foundry waste in utilisation and disposal

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In this work the harmful compounds of most commonly used foundry sands in Finland, i.e. green sand, furan sand, ester hardened phenolic sand and sodium silicate sand together with respective dusts were identified. Their environmental impact was evaluated mainly by comparing the content of harmful compounds against target values given for non-contaminated soil. Additionally, an interlaboratory comparison study was arranged in order to get information on the comparability of the metal and polycyclic aromatic hydrocarbons (PAHs) analysis results.

The total Chromium contents of studied foundry sand and dust types generally exceeded significantly the target values given for the evaluation of contaminated soil. However, the leaching of Chromium was as a whole very low. Additionally, foundry sands contained only small amounts of organic compounds compared to the target values given for the contaminated soils. On the other hand in case of foundry dusts phenol concentrations correlated with PAH-concentrations resulting in significant phenol and PAH-concentrations in some dust types. For detailed environmental evaluation further information on the leaching behaviour of different metals from foundry dusts is required, especially when the waste masses are relative big. Results of the interlaboratory comparison, especially for some metals as aluminium and chromium, varied significantly addressing the need for further discussions on advantages and disadvantages of different test methods.

1. INTRODUCTION

Among Finnish foundry industry approximately 130.000 tons of excess foundry sands are annually generated. Despite the relative high recycling rates of foundry sands in the most foundries for every produced ton of iron and steel one ton of excess foundry sand is produced. The current recycling rates of foundry sands vary between 50 % and 90 % depending on resin type, regeneration method and the metal type to be casted. In addition to excess foundry sands in nearly every process stage of casting varying amount of dust with different composition particle size is also formed.

Reliable information on harmful compound content and on environmental impact of different foundry wastes are needed for their classification (hazardous/non-hazardous waste), disposal and utilisation decision-making purposes. Currently, these decisions are made mainly on the basis of total compositions, which could in future also serve as a basis for the possible classification of foundry waste. However, reliable information on average foundry waste compositions and analytical quality of results is still lacking. Also the Dust and Sludge Group active under Thematic Network Foundry Waste emphasised the need for quality assurance of analytical methods used in characterisation of foundry waste in it's meeting held in May 1998 in Finland.

The main aim of this work was to identify the harmful compounds of the most commonly used foundry sands in Finland i.e. green sand, furan sand and ester hardened phenolic sand together with respective dusts. Secondly, their environmental impact was evaluated, mainly by comparing the content of harmful compounds to target values given for non-contaminated soil. Additionally, as a result of discussions among the Thematic Network Foundry Waste also an interlaboratory comparison using foundry dusts was arranged in order to get information on the comparability of the metal and polycyclic aromatic hydrocarbons (PAHs) analysis results.

2. MATERIALS AND METHODS

2.1. Environmental properties of foundry waste

Selected foundry waste types are shown in Table 1. All studied foundry waste samples were made from sub-samples collected at respective foundries according to a pre-sketched sampling strategy.

Table 1
Selected foundry waste types

Sand type	Sample code
Green sand	Sand 1
	Sand 2
	Sand 3
	Dust 1 (sand preparation)
	Dust 2 (unloading)
	Dust 3 (steel grit blasting)
Furan sand	Sand 5
	Sand 6
	Sand 13
	Dust 4 (emptying and regeneration of casting moulds
	Dust 5 (chromite sand extraction)
	Dust 6 (steel grit blasting)
Ester hardened phenolic sand	Sand 7
	Sand 8
	Sand 9a
	Sand 9b
	Dust 7
Waterglass sand	Sand 12

The studied foundry waste characteristics were selected on the basis of harmful compounds in sand binding agents. Chemical composition of selected metals i.e. Cr for sands and As, Cd, Co, Cr, Cu, Pb and Zn for dusts, polyaromatic hydrocarbons (PAHs) and phenol concentrations were determined for each foundry waste sample. Also eluate pH was measured. Additionally, for sand samples some analyses of isocyanate and N,N-diethylamine together with screening of organic compounds were carried out. The studied characteristics and the used analysis methods were the following:

Characteristic	Method	Note
Eluate pH	The mixture of sand and de-mineralised water in (liquid/solid-ratio 1:10) is shaken for 10 min.	Describes the acidity of the material i.e. acidic eluate indicates excess of used acid.
Ignition loss	The sample is annealed at 550 °C.	Indicates the amount of incombustible binding agents.
Metal concentrations	Microwave assisted dissolution (HNO_3, HF, H_2O_2) followed by insoluble fraction treatment using lithiumtetraborate as a fluxing agent and subsequently analysis with FAAS.	
Polyaromatic Hydrocarbons (PAHs)	Determination of 31 PAHs from dichloromethane extract with GC-MSD using SIM-technique and internal standards. The clean up of extracts is made with Silica column chromatography. The determination limit is 0,01 mg/kg and the uncertainty ±30 %.	The amount of PAHs indicates the amount of incombustible binding agents. Tens of PAHs are known. Usually 10-16 compounds are determined. The most common compound is Naphtalene. The most harmful for environment is Benzo(a)pyrene).
Phenol concentration	A sample is mixed with water and the mixture is distilled using steam. Phenol concentration is determined from distillate according to SFS3011.	There are several phenol compounds. Phenols are usually determined as a total amount e.g. Phenol-index.
Screening of organic compounds	Determination from dichloromethane extract using GC-MSD -analysis.	
Formaldehyde	Reaction between formaldehyde and acetylacetone with subsequent spectrophotometric determination	
Isocyanates and N,N-Diethylamine	LC-UVD/ECD – analysis and GC-FID -analysis.	As components of binding agents their concentration describes the possible inactive binding agent.

Based on total composition data leaching behaviour of selected foundry waste samples was also evaluated. Three different leaching test types were utilised in the assessment of the leaching behaviour of studied foundry wastes. The pH-dependent leaching behaviour of certain metals i.e. Cr for sands and Cr, Cu, Pb and Zn for dusts, from selected samples were characterised using pH-static test. For dust samples the leaching behaviour was tested only at pH-value 4, which simulates the extreme conditions in the environment. Additionally, the leaching behaviour of selected dust samples and two sand samples in short and medium period was evaluated by performing batch shaking tests and column tests. The principles of the leaching tests were the following:

The CEN-test	This test developed by CEN (European Committee for Standardization) is a batch leaching test producing eluates which shall be analysed chemically and physically. The test gives a rough estimate of the amount of inorganic components leaching into the environment from waste materials. The test sample with the particles less than 4 mm (95 %) and 10 mm (100 %) is mixed with demineralised water (pH 4) under defined test conditions. The test procedure comprises two leaching steps i.e. at L/S = 2 and L/S = 2 - 10. The residue from the leachant(s) is separated by filtration and the properties of the eluate(s) are measured. The test is based on the assumption that equilibrium or near-equilibrium is achieved between the liquid and solid phases during the test period. The leaching of inorganic components from powdered and granular materials (the size of) is interpreted as a function of the value of L/S. L/S is the quotient of the cumulative volume of leachant and the mass of the material exposed to leaching (expressed in l/kg).
Column test	The aim of the column test developed in the Netherlands (NEN7343) is to simulate the leaching of inorganic components from powdered and granular materials in an aerobic and water saturated environment as a function of the value of L/S. L/S is the quotient of the cumulative volume of leachant and the mass of the material exposed to leaching (expressed in l/kg). In the column test the leaching liquid (acidified water) is passed through the material to be tested, whereby after set quantities of leaching liquid have been passed through it, the concentrations of the leached components in the eluate are measured. The leached quantity can be calculated based on the compound concentrations in the eluates for each component analysed both per fraction collected and cumulatively. The pH-value of the eluate is dictated by the material itself.
The pH-static test	The pH static test is a tool to determine the influence of pH on the leaching behavioiur. The pH conditions in the environment are usually the most significant factor influencing the leaching behaviour. A small change in pH can lead to a significant change in leachability. The pH static test is carried out by mixing material with water at a liquid to solid ratio L/S 10. The pH of the mixture is kept for 24 hours at the specific pH (4 - 12) by addition of nitric acid or sodium hydroxide. After the leaching procedure, the solid residue is separated by filtration and the concentrations of the leached components in the eluate are measured. (prEN 12457-3)

2.2. The interlaboratory comparison

The invitation concerning the comparison was sent to 17 partner organisations of Thematic Network - Foundry Waste. Total of 12 answers was received including three declinations.

Two dust types with presumably different concentration levels were selected for this comparison: sand dust and melting dust. The sampling of dusts was carried out by the source foundries. The characteristics of the dusts were the following:

	Sand dust	Melting dust
Process source	Decoring and recovery - silo unloading	Smelter filter
Sample preparation	Mixing of 150 g from each sub-sample Division of bulk sample (1.4 kg) into 16 final comparison samples using a laboratory sample divider	Division of sample (1.4 kg) into 16 final comparison samples using a laboratory sample divider

The participating laboratories with respectively available analysis methods analysed three parallel samples of each dust sample type for their total concentrations of eight defined metals (Al, As, Cd, Co, Cr, Cu, Pb and Zn) and for polycyclic aromatic hydrocarbons (16 EPA-PAH). No normalisation of the analytical methods was attempted to attain in order to gain information on present practice and possible differences between available methods. A summary of the analytical procedures used by different laboratories are presented in Appendices 1 and 2.

3. RESULTS

3.1. Environmental properties of foundry waste

The obtained concentrations of harmful compounds in studied foundry waste samples are compiled in tables 2-3.

Table 2a

Chemical compositions of studied foundry sand samples (concentrations in mg/kg)

	Green sand			Furan sand			Ester hardened phenolic sand				Waterglass sand
	Sand 1	Sand 2	Sand 3	Sand 13	Sand 5	Sand 6	Sand 7	Sand 8	Sand 9A	Sand 9B	Sand 12
Eluate pH	9.5	9.7	9.8	4.4	4.9	3.2	7.8	9.2	9.7	9.3	10.1
Chromium (Cr)	6300	4400	<100	30000	14000	14500	2600	<300	1300	8700	<100
Phenol	7	20	3	0,5	1,1	0,7	5	10	3	0.8	<0.05
Formaldehyde	< 20						< 20				
PAHs	9.1	28	18	0.1	1.0	0,2	0.7	2.7	1.2	1.7	0.4
MDI $^{1)}$	< 5	< 5	< 5				< 5	< 5	< 5	< 5	

$^{1)}$ Diphenylmethanediisocyanate, $^{2)}$ Isoforonediisocyanate, $^{3)}$ Diethylamine

Table 2b

Chemical compositions of studied foundry dust samples (concentrations in mg/kg)

	Dust 1	Dust 3	Dust 3	Dust 4	Dust 5	Dust 6	Dust 7
Eluate pH	9.9	8.9	10.1	6.6	5.1	9.6	10.3
Phenol	48	184	5	19	1.2	0.8	51
Aluminium (Al)	65000	42000	16000	82000	61000	81000	
Arsenium (As)	11	6	4	5	<2	10	
Cadmium (Cd)	0.3	0.2	<0.1	5	1,5	0.2	0.21
Cobalt (Co)	<10	<10	30	51	130	100	<10
Chromiun (Cr)	1100	2500	8100	29000	123000	85000	2400
Copper (Cu)	27	30	590	810	430	790	69
Lead (Pb)	38	26	5	460	150	76	41
Zinc (Zn)	130	130	100	1800	790	510	140
PAHs	81	88	6.6	82	14	3.3	80

Table 3
Chemical screening of organic compounds for foundry sands

Sample	Identified compounds (excluding PAHs)
Green sand	
Sand 1	• Fat acids (hexadecane acid methyl esters and 9-octadecene acid methyl ester)
	• Hydrocarbons C_{15}-C_{20}
	• Phtalates
Sand 2	• Phenols (Phenol and alkylphenols)
	• Cyclic ketone: 3,3,5-trimethylcyclohexenone
	• hydrocarbons (C_{14}-C_{27}) (high concentrations)
	• Hexadecane acid
	• Phtalates
Sand 3	• Phenols (Phenol and alkylphenols)
	• Cyclic ketone: 3,3,5-trimethylcyclohexenone
	• Hydrocarbons (C_{15}-C_{27}) (high concentrations)
Furan sand	
Sand 13	• Hydrocarbons
Sand 6	• Benzaldehyde (main component)
	• Benzylalcohol
	• Sulfonyl derivatives (DI-p-tolylsulfone and respective benzene derivative)
	• Dicarboxylic acid esters
	• Glycolic derivatives
Ester hardened phenolic sand	
Sand 7	• Benzaldehyde
	• Benzylalcohol
	• Ketone (possibly 1-asetylokis-propanone, remarkable concentration)
	• Esters (dikarboxylic acid ester, propanetriol di-,triasetates)
	• Small amouts of phenols
	• Small amounts of glycolic derivatives
Sand 8	• Benzaldehyde
	• Phenols
	• Propanetriol asetates
Sand 9A	• Benzaldehyde
	• Dihydrofuranone
	• Benzylalcohol
	• Phenols (small amounts)
	• Glycolic ethers. E.g. 2-(2-butoxyetoxy)-ethanol
	• Fat acid esters
	• Propanetriol asetates
Sand 9B	• Benzaldehyde
	• Dihydrofuranone
	• Glycolic ethers
	• Fat acid esters
	• Propanetriol asetates
Waterglass sand	
Sand 12	• Hydrocarbons

Results of leaching tests are shown in Tables 4 and 5. Due to the difficulties in achieving the equilibrium conditions at pH-value 4 the target pH for the dust sample 6 was set at 6. Redox-values, which are supposed to indicate chemical changes in material during the leaching process, are also shown in respective table although the assessment of causal connection between redox-values and leaching behaviour is at the moment not yet established. Conductivity is a routine measurement in the case of water analysis and it describes ion strength.

Table 4
Leaching of chromium from selected foundry waste samples in different pH-values

	Ester hardened phenolic sand	Furan sand								
	Sand 7 mg/kg	Sand 13 mg/kg	Dust 4 mg/kg				Dust 5 mg/kg		Dust 6 mg/kg	
pH	Cr	Cr	Cr	Cu	Pb	Zn	Cr	Zn	Cr	Cu
3.0	0.06									
4.0			1.6	45	6.3	200	0.55	67		
4.5 (sample pH)		0.12								
4.7	0.01									
6.0	0.09	0.14							0.06	<0.1
7.0	0.08	0.47								
7.6 (sample pH)	0.03									
7.6 (sample pH)	0.02									
9.0	0.06									
10.0	0.33									
12.2	0.19									

Table 5
Results from column and batch shaking tests (cumulative amount mg/kg)

	Ester hardened phenolic sand		Furan sand			
	Sand 7 mg/kg		Sand 13 mg/kg		Dust 1 mg/kg	
	L/S 2	L/S 10	L/S 2	L/S 10	L/S 2	L/S 10
pH	7.7	8.1	6.0	6.2	8.3	8.7
Redox, mV	340	660	340	390	360	380
Conductivity, mS/m	15	4	35	10	1450	220
Chromium, mg/kg	0.007	< 0.02	< 0.04	< 0.05	0.03	< 0.1
Copper, mg/kg					0.19	< 0.2
Lead, mg(kg					< 0.05	< 0.2
Zinc, mg/kg					< 0.05	< 0.2

3.2. The interlaboratory comparison

All together, nine laboratories from nine countries, participated in the foundry dust comparison analysing at least the metals. PAH-analysis was carried out in five laboratories.

Cochran's and Grubbs' tests (ISO 5725-2:1994) were used for testing the outliers in data. After that, the average concentration and standard deviation were calculated. A single value was called a statistical outlier if the test statistic was greater than 1 % critical value of test in question. Summaries of comparison results after statistical analysis for sand dust and melting dust are shown in tables 6 and 7.

Table 6
Summary of comparison results for metals in dusts

	Sand dust						Melting dust					
	Mean mg/kg	Std.Dev. mg/kg	C.V. %	N	Min. mg/kg	Max. mg/kg	Mean mg/kg	Std.Dev. mg/kg	C.V. %	N	Min. mg/kg	Max. mg/kg
Al	33 666	28 543.7	85	23	14 900	87 700	4 756	2 405.0	51	23	2 400	10 000
As	3	0.6	18	4	3	4	68	17.9	26	23	52	114
Cd	4	2.3	56	17	1	9	56	12.0	21	25	42	84
Co	32	12.0	37	23	19	57	64	20.6	32	25	31	100
Cr	2 272	16 798.1	739	22	280	37 000	101	66.7	66	25	33	241
Cu	690	82.8	12	21	555	830	1 612	277.8	17	23	1 285	2 283
Pb	401	95.2	24	25	286	591	2 825	429.9	15	25	2 255	3 952
Zn	1 685	330.5	20	23	1 249	2 454	124 677	13 018.5	10	25	103 200	151 365

Table 7
Summary of comparison results for PAHs in dusts

	Sand dust						Melting dust					
	Mean mg/kg	Std.Dev. mg/kg	C.V. %	N	Min. mg/kg	Max. mg/kg	Mean mg/kg	Std.Dev. mg/kg	C.V. %	N	Min. mg/kg	Max. mg/kg
Naphtalene	14.20	5.23	37	14	4.52	21.76	0.95	0.60	63	11	0.40	1.77
Acenaphtylene	0.87	0.60	69	11	0.35	2.00	0.27	0.15	55	7	0.15	0.46
Acenaphtene	3.56	1.40	39	14	1.60	5.94	0.21	0.35	165	13	0.03	1.00
Fluorene	4.04	2.47	61	11	1.30	9.49	0.64	0.49	77	13	0.26	1.80
Anthracene	1.71	1.74	102	14	0.13	5.20	0.84	0.23	27	14	0.44	1.11
Phenantrene	8.17	4.44	54	14	1.20	16.44	4.14	1.02	25	14	2.00	5.5
Fluoranthene	2.05	0.99	48	11	0.11	4.08	8.37	1.94	23	14	5.70	10.76
Pyrene	0.83	0.68	82	10	0.05	2.13	8.77	1.30	15	14	6.00	10.43
Benzo(a)anthracene	0.06	0.07	109	6	0.01	0.19	3.09	2.07	67	11	0.10	6.64
Chrysene	0.05	0.07	137	3	0.02	0.16	4.92	1.45	30	11	2.50	6.80
Benzo(b)fluoranthene	0.14	0.03	22	6	0.11	0.17	5.44	2.13	39	10	3.57	9.70
Benzo(k)fluoranthene	0.03	0.04	132	4	0.01	0.09	4.10	3.17	77	14	0.93	9.37
Benz(a)pyrene	0.11	0.03	26	1	0.07	0.13	3.39	1.03	30	14	1.70	4.97
Dibenzo(a,h)anthracene	ND	-	-	1	-	-	1.50	1.27	85	10	0.47	3.87
Indeno(1,2,3-cd)pyrene	ND	-	-	1	-	-	3.31	1.20	36	14	1.10	5.90
Benzo(ghi)perylene	ND	-	-	1	-	-	1.77	1.73	98	14	0.26	5.05
Sum of PAH	42	12.2	29	13	22.69	62.87	56.55	11.35	20	13	27.00	77.00

ND = could not be determined, *Lab. 3: Dibenzo(a,h)anthracene and indeno (1,2,3-cd)pyrene determined together, *Lab. 4: Chrysene and triphenylene determined together, *Lab. 6: Benz(b)fluoranthene and benz(k)fluoranthene determined together, *Lab. 7/2: Benz(b)fluoranthene and benz(k)fluoranthene determined together

4. DISCUSSION AND CONCLUSIONS

4.1. Environmental properties of foundry sands

According to the obtained results the total Cr-concentrations of the studied foundry sands were generally relatively high compared to the target values given for the contaminated soils. PAH-concentrations did not correlate with phenol concentrations, but they correlated with other residual compounds and were dependent on the sand type. In green sands, especially benzo(a)pyrene-concentration in the sand sample 2, PAH-concentrations were significant, whereas for furan sands PAH-concentrations were low. Ester hardened phenolic sands contained small amounts of PAHs, especially naphtalene.

Obtained formaldehyde concentrations for different sand types were not significant. In the screening analysis no isocyanates and harmful compounds were observed. However, eluates of furan sands were acidic.

The leaching of Cr from ester hardened phenolic sand and furan sand was very low at all pH-values studied. Also in column tests the leaching of chromium from sand samples was insignificant (< 0.5 mg/kg).

4.2. Environmental properties of foundry dusts

The obtained results indicated significant total concentrations of Cr with varying amounts of phenols and PAHs for all studied foundry dust samples. Contrary to foundry sands phenol concentrations of foundry dusts seemed to correlate with PAH-concentrations resulting the highest phenol concentrations in those dusts i.e. green sand dust and ester hardened phenolic sand dust samples with significant PAH-concentrations. Additionally, phenol and PAH-concentrations of dusts seemed also to vary strongly according to sampling site i.e. process stage.

Based on the total composition analyses leaching behaviour was assessed only for furan sand dusts. Only for furan sand dust sample 1 (emptying and regeneration of casting moulds) some leaching of Cu and Zn was observed, whereas the leaching of Cr and Pb was low.

4.3. The interlaboratory comparison

The obtained interlaboratory results indicated significant influence of various methods on the test results. All participating laboratories used different analytical and destruction methods and the results, especially for some metals as aluminium and chromium, varied significantly. However, laboratories using comparable analytical methods reported results of the same magnitude. Variation range of the replicates within one laboratory was also typically relative small, usually less than 10 % of the mean value. Besides the analysis method the variation of results seemed to be dependent on the sample type, as the sand dust results appeared to vary more than melting dust results. The sand dust sample was collected from a foundry where chromite sand is used in the moulding process. Main elements of chromite sand are Si, Fe, Al, Cr and Mg, usually appearing as silicates and oxides.

The usage of fluxing agents in decomposition gave highest values for Al- and Cr-concentrations. Also the use of HF in both microwave assisted digestion and acid digestion with boiling significantly increased concentration results for Al, Co, Cr, indicating that HF possibly decomposes the sample matrices. In case of Cu-analysis microwave assisted digestion with HF gave higher concentration values than aqua regia or acid digestion.

PAH-analysis was carried out as expected only by few laboratories. Variation range of the replicates within one laboratory in PAH-analysis seemed to be slightly larger than in the case of metal analysis. All laboratories also used different extraction solvents and different clean-up procedures, which resulted in rather large variations in the results between different laboratories. Differences were mainly observed in concentrations of naphtalene, anthracene, phenantrene and benz(a)pyrene. Analysis of naphtalene is demanding due to risks of volatilisation and Benz(a)pyrene in a compound of special interest due to its carcinogenity. However, due to small amount of data obtained in this comparison very detailed conclusions based on these PAH-results can not be made.

5. FUTURE WORK

Generally, the results of the interlaboratory comparison indicated the need for further discussions on advantages and disadvantages of different test methods, although in some cases the variations between different laboratories were relative small and laboratories using methods based on the same principles mainly obtained almost comparable test results. For some metals the results however varied significantly, for example with a factor of 5 and 100 for Al and Cr, respectively. This was apparently due both to the use of different reagents (acids, fluxing agents, oxidising agents) and to different test conditions (e.g. boiling, microwave assisted digestion). Currently more attention has been paid to metal analysis. In future, more information on organic pollutants will however be required.

The total Chromium contents of studied foundry sand and dust types generally exceeded significantly the target values given for the evaluation of contaminated soil. However, the leaching of Chromium was overall very low. Additionally, for foundry sands the content of other harmful compounds was relatively low compared to the target values given for the contaminated soils. On the other hand in case of foundry dusts phenol concentrations correlated with PAH-concentrations resulting in significant phenol and PAH-concentrations in some dust types. For detailed environmental evaluation further information on the composition variations of foundry wastes and the leaching behaviour of different metals from foundry dusts are required, especially when the amount of dust is relative big.

Table 8

Metal analysis. Sample preparation methods and analytical procedures used by the participants in the interlaboratory comparison

Lab. Nr.	Sample preparation	Analytical procedure	Uncertainty estimation	Reference
1	◆ Aqua Regia dissolution ➢ SiO_2-separation ➢ Decomposition using HF, HNO_3 + HCl + H_2O, $HClO_4$, Li_2CO_3 + $Li_2B_4O_7$, $K_2S_2O_7$	FAAS (PE 2100) with known addition	± 10 %	Not reported
2	◆ Aqua Regia digestion ➢ 3 g of dried sample + 28 ml acid ➢ Several hours at room temperature ➢ Boiling for 2 h ➢ Filtration	ICP-OES / Varian (Liberty 2000)	Not reported	DIN 38 414/7: Sludge and sediments – Digestion using aqua regia for subsequent determination of the acid soluble portion of metals
3	◆ Aqua Regia extraction ➢ 3 g of dried sample + 28 ml acid ➢ Standing at room temperature for 16 h ➢ Boiling under reflux for 2 h ➢ Filtration	ICP-AES ICP-MS	Not reported	ISO/DIS 11466: Soil quality – Extraction of trace metals soluble in aqua regia EPA 6010A: ICP-AES EPA 6020: ICP-MS
4	◆ Microwave assisted digestion (HNO3 + HF + H_2O_2): Cd, Cu, Pd, Zn (Cr) ◆ Insoluble fraction treatment using $Li_2B_4O_7$ as a fluxing agent: Co, (Al, Cr)	ICP-AES (As with GFAAS)		
5	◆ Acid dissolution (HNO_3 + HF)	ICP-OES	Not reported	Not reported
6	◆ Acid dissolution (HNO_3)	ICP-AES (external calibration)	< 10 %	Not reported

Table 8

Metal analysis. Sample preparation methods and analytical procedures used by the participants in the interlaboratory comparison

Lab. Nr.	Sample preparation	Analytical procedure	Uncertainty estimation	Reference
7	Lab. 1 ♦ Acid dissolution (HNO_3)	ICP-AAS	Not reported	SS 02 81 52: Vattenundersökningar - Atomabsorptionsspektrometri i flamma - Speciella anvisningar för aluminium, bly, järn, kadmium, kobolt, koppar, krom, mangan, nickel och zink. SS 02 81 83: Vattenundersökningar - Metallhalt i vatten, slam och sediment -Bestämning med atomabsorptionsspektrometri - Elektrotermisk atomisering i grafitugn - Allmänna principer och regler. SS 02 81 84: Vattenundersökningar - Metallhalt i vatten, slam och sediment - Bestämning med flamlös atomabsorptionsspektrometri - Speciella anvisningar för aluminium, bly, järn, kadmium, kobolt, koppar, krom, mangan och nickel.
	Lab. 2 ♦ Microwave assisted digestion (HNO3 + H_2O_2)	ICP-AES (As with GFAAS)	Not reported	
8	♦ Microwave assisted acid digestion ➢ 0.5 g of sample + 9 ml HNO_3 + 3 ml HF ➢ Heating in microwave system ➢ Temperature program: 180± 5 °C in 5.5 min. + at 180± 5 °C for 9.5 min. ➢ Centrifugation	♦ ICP-MS	10 %	EPA 3052/96: Microwave assisted acid digestion of siliceous and organically based materials EPA: 200.8/93: Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma - Mass Spectrometry
9	♦ Aqua Regia dissolution	♦ ICP-OES (Al, As, Cr, Cu) ♦ FAAS (Cd, Co, Pb, Zn)	± 3 %	Not reported

Table 9

PAH analysis. Sample preparation methods and analytical procedures used by the participants in the interlaboratory comparison

Lab. Nr.	Sample preparation	Analytical procedure	Uncertainty estimation	Reference
1	Not participated			
2	Not participated			
3	♦ Soxhlet extraction (dichloromethane / acetone)	♦ GC-FID ♦ Column: DB-5	Not reported	EPA 8100
4	♦ Soxhlet extraction (toluene) ♦ DMSO-liquid-liquid partitioning ♦ Silica cartridge clean-up ♦ Final solvent: n-hexane	♦ Quadropole GC-MS (HP 5970, HP 5890) ♦ Column: DB-17 (silica, 30 m, 0.25 mm) ♦ Detection technique: SIM ♦ Quantitation: Internal Standard Method with 3 compounds	± 30 %	VTT/KET1200395, accredited method (FINAS)
5	Not participated			
6	♦ Soxhlet extraction (dichloromethane) with internal standards	♦ GC-MS ♦ Detection technique: SIM	5-10 %	Not reported
7	Lab. 1 ♦ Extraction + clean-up	♦ GC (SNV 3829)	Not reported	Not reported
	Lab. 2 ♦ Extraction (pyrophosphate + ethylacetate/cyclohexane) with internal standard ♦ Cenrifugation	♦ GC-MS (HP 5970, HP 5890) ♦ Column: PE-5 (20 m, 0.18 mm, 0,18 µm) ♦ Detection technique: SIM ♦ Quantitation: Internal Standard Method with 3 compounds	10-30 %	Nordtest Tech. Report 329
8	♦ Pressurised fluid extraction (PFE)	♦ GC-MS	10 %	EPA 3545/96: Pressurized fluid extraction (PFE) EPA 8270/96: Semivolatile organic compounds by gas chromatography / mass spectrometry (GC/MS)
9	Not participated			

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Leaching of PCBs and Chlorophenols from contaminated soil and waste - Influence of leaching test characteristics

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Organic contaminants are found in soil at sites where chemicals containing organics have been used or handled. Sites contaminated with chlorophenols are a typical problem in Finland due to their large use as wood preserving agents at saw mills. The major compounds identified in the contaminated soils are tetrachlorophenols and pentachlorophenols. PCBs were used in the 1960s and 1970s in polysulphides containing sealing compounds for wall elements. The PCB-contents in these compounds were at least 20 % resulting in PCB contamination in soils near the wall elements. PCB-contaminated soils can also be caused from leackage of PCB-condensers. PCBs and Chlorophenols have been chosen in this study as typical organic contaminants with different chemical properties.

The aim of this study was to assess the effect of leaching test characteristics on test results for Chlorophenols and PCBs. Furthermore, the effects of some relevant environmental factors controlling the leaching behaviour were evaluated. The study was especially focused on practical aspects aiming to test conditions ensuring reproducible test results. In particular, the influence of filters and the needed equilibrium time for the leaching process were studied.

The work was a part of the EU-project "Development of standard leaching tests for organic pollutants in soils, sediments and granular waste materials" co-ordinated by ECN (contract SMT4-CT97-2160). The results will give background data for development of standardised leaching test methods for some organic contaminants.

1. INTRODUCTION

The leaching behaviour of organic contaminants, like PCBs and Chlorophenols is controlled by a number of factors, pH, DOC and ionic strength. Sorption has also been recognised as having a fundamental role in retarding the movement of organic compounds. The most important soil properties for sorption are: organic matter content, clay content, pH value and cation exchange capacity. Further parameters influencing the leaching are: porosity of the soil, water holding capacity, macropores and crevices and plant cover. The mobility of organic contaminants is controlled by a number of environmental, hydrological, and climatic variables, such as temperature, pH of the environment and the amount of water. Especially, the colloidal transport of organic contaminants plays an important role.

Substantial methodology problems arise in determining the leachability of organic contaminants, since they are easily lost because of sorption onto leaching test apparatus, during leachate storage and during the separation of the dissolved and particulate phase (Rood *et al* 1994). Additionally, hydrophobic compounds desorbed from the soil into the leachate are subjected to chromatographic effects during further passage in the soil column.

Hydrophobicity often plays an important role in describing and explaining the fate of many contaminants. Hydrophobic properties of a compound are usually measured by an equilibrium distribution ratio between two different physicochemical phases, such as octanol/water partitioning. Since partitioning is, however, not entirely regulated by interactions in the aqueous layer of the two phase systems, it seems more appropriate to use aqueous solubility as a hydrophobicity parameter. Nevertheless, the exact nature of hydrophobic interactions has been under heavy discussion. (Opperhuizen *et al* 1988)

The aqueous solubilities of PCBs are very low ranging from 2.7 ppb to 3500 ppb for commercial mixtures (Aroclor®). A considerable volume of data has been published on PCB solubilities, but discrepancies exist because of the experimental difficulty of generating and handling such dilute solutions. (Chou & Griffin (1986),Mackay *et al* 1980, Shiu & Mackay 1986)

In general, polar organic compounds are more water soluble than nonpolar compounds of similar molecular size. Moreover, the compounds containing hydroxyl groups (alcohols and phenols) are usually more soluble than similar compounds containing ketone functionalities. As Chlorophenols consist of both polar and non-polar portions; they are transitional between hydrophobic and hydrophilic, their hydrophobicity, with log K_{ow} values ranging from 2 to 4, is considerably lower than corresponding values for PCBs (Liu & Chang 1997). The aqueous solubilities of Chlorophenols depend primarily on three factors i) the molecular size and shape which can be characterised by molar volume, ii) the melting point in the case of solids, and iii) the extent of dissociation as determined by pH, pK_a, and ionic strength. The tendency of Chlorophenols to dissociate in aqueous solution increases as the number of chlorine atoms increases. (Ma *et al* 1993)

pH has been found to greatly affect the sorption of ionisable organic compounds e.g. chlorophenols, since the pH affects not only the speciation of compounds but also the surface characteristics of natural solids (e.g. surface charge and potential). At neutral pH, the overall sorption has been found to be dominated by sorption of the dissociated fraction. (Jacobsen *et al* 1996, Shimizu *et al* 1992)

Pentachlorophenol is a weak acid (pK_a = 4.7) existing in two chemical forms in aqueous solution: a relatively apolar and slightly soluble phenol (PCP^0) and the dissociated form, a highly soluble phenolate ion (PCP^-):

$$PCP^0_{(aq)} + H_20 \Leftrightarrow PCP^-_{(aq)} + H_3O^+_{(aq)} \qquad (1)$$

In an aqueous system the equilibrium can be calculated from the pK_a of PCP:

$$pH = pK_a + \log([PCP^-]/[PCP^0])$$

or

$$[PCP^0] = [PCP_{tot}] + (1 + 10^{pH-pK_a})^{-1}$$

where PCP_{tot} is total PCP. At pH 7 the equilibrium shifts to the right, that is 99.4 % of the total amount of PCP is in dissociated form (PCP^-). In general, the phenolic structure is thought to be more toxic than the charged analogue due its tendency to sorb to biological membranes. For pH <7, PCP sorption increases with an increase in the fraction of neutral species as the pH decreases. For pH > 7, sorption of phenolate ion and the formation and sorption of the neutral metal-phenolate ion pair must be taken into account. (Lee *et al* 1990, Rutgers *et al* 1998)

2. MATERIALS AND METHODS

2.1 Soil samples

For the leaching tests, the target concentration levels in leachates should be at least 10 times the detection limit. Unforeseen difficulties were encountered in finding appropriate sample materials. Several real waste and soil materials were tested, but rejected due to sample heterogenity, low leachability of contaminants or too small an amount of sample for testing. Only a few tests could be performed with real contaminated soils. The real PCB sample was prepared from several separate humus rich samples from soils near wall elements containing PCB sealing compounds. The sample was calculated to contain 30 ppm PCBs. Some real chlorophenol samples were taken from saw mills where wood preservation agents had been used .

In addition to real contaminated soil materials, two types of soil samples, humus rich (humus content 26 %) and sandy, were spiked with PCBs and chlorophenols, respectively. A stock solution prepared from chlorophenol containing preservation agents with main components of 2,4,6-trichlorophenols, 2,3,4,6-tetrachlorophenols and pentachlorophenol was used for spiking the chorophenol contaminated soils. PCB contaminated soil samples were prepared using Arochlor 1260. The spiking solutions were diluted in hexane. The spiked samples were prepared in batches of 1-4 kg by mixing the soil sample and spiking solutions for 24 hours (chlorophenols) and 48 hours (PCBs). Two concentration levels were chosen, 50-100 mg/kg and 1000 mg/kg. The compositions of the soil samples are presented in Table 1.

Table 1.
Composition of spiked samples.

Contaminant	**Soil**	**Characteristics of the soil**	**Concentrations of contaminants**
Chlorophenols 90 mg/kg	Sandy soil	Humus content 0 %, maximum grain size < 1mm	• *2,4,6-trichlorophenol: 28 mg/kg* • *2,3,4,6-tetrachlorophenoli: 17 mg/kg* • *Pentachlorophenols: 45 mg/kg*
Chlorophenols 120 mg/kg	Humus rich soil	Water extract pH 5,3, Humus 25,7%	• *2,4,6-trichlorophenol: 43 mg/kg* • *2,3,4,6-tetrachlorophenoi: 17 mg/kg* • *Pentachlorophenol: : 60 mg/kg*
Chlorophenols 1400 mg/kg	Humus rich soil	Water extract pH 5,3, Humus 25,7%	• *2,4,6-trichlorophenol: 400 mg/kg* • *2,3,4,6-tetrachlorophenoi: 320 mg/kg* • *Pentachlorophenol: : 660 mg/kg*
PCBs 60 mg/kg	Humus rich soil	Water extract pH 5,3, Humus 25,7%	*Arochlor 1260*

2.2 Methods

2.2.1 Analytical methods and apparatures

PCB-compounds were determined with gaschromotographic techniques (GC-ECD) from the hexane extract. 2,4,6-tribromibiphenyl was used as an internal standard. The uncertainity has been estimated to be ± 30 %. The following congeners were determined:

PCB-congener	IUPAC-number
2,2',5,5'-tetrachlorobiphenyl	52
2,2',4,5,5'-pentachlorobiphenyl	101
2,3',4,4',5-pentachlorobiphenyl	118
2,2',3,4,4',5'-hexachlorobiphenyl	138
2,2',4,4',5,5'-hexachlorobiphenyl	153
2,2',3,4,4',5,5'-hexachlorobiphenyl	180

The sum of PCBs was calculated according to the formula:

Total PCBs $=2{,}7 \times \sum_{52}^{180} c_i$, where c_i is the concentration of the determined PCB congener .

Chlorophenols were determinated with gaschromatographic technique(GC-ECD). Prior to analysis samples were extracted with acidic diethylether (pH 2) followed by the acetylation of chlorophenols. 2,4,6-tribromophenol was used as internal standard. The uncertainity of the method was estimated to be ± 30 %.

A laser-based particle size distribution analyser (Coulter with a measurement range of 0,2-1000 μm) was utilised in order to understand the influence of fine particles on the leaching concentration of PCBs and Chlorophenols.

Centrifugation was performed for 0,5 h at 4000 rpm (Heraeus Cryoge Fuge M700).

2.2.2 *Leaching test methods*

The results were interpreted on the basis of liquid (L) to solid (S) ratio achieved in the tests. Batch leaching tests were performed with one or two leaching steps (modifications of prEN 12457). In the one leaching step test the sample was mixed at L/S 10. In the two leaching step procedure the sample was mixed first with water at L/S 2. The eluate and the solid was separated and the solid was mixed with fresh water subsequently at L/S 8.

The pH environment may change with time, e.g. due to carbonation. pH static tests were carried out to characterise the pH-dependent leaching behaviour for the selected contaminants. The tests were performed at L/S 10 under pH-controlled conditions using automated pH control equipment with nitric acid addition.

The eluates collected from the leaching tests were analysed. From the leachates PCB/Chlorophenol concentration, pH, and conductivity are determined.

2.2.3 Test arrangements

The filter sorption assessment on leachate concentrations of organic contaminants was carried out by testing different filter types (See Table 2). The results from the filters were also interpreted according to the particle distribution in the eluate after filtration. This gives an indication of the particle bound contaminants in the eluate. The effects of filtration technique on possible volatilisation of organic contaminants and resulting concentration losses in leachates were evaluated by two different filtration techniques, vacuum and pressure filtration. These were used in parallel in some batch shaking tests. Also centrifugation was studied as a pretreatment step before filtration.

Table 2.
The tested commercial filters.

Manufacturer	Trade mark	Filter material	Application	Filter diameter mm	Pore diameter µm
1. Schleicher & Schuell	589 Blauband/Blue	Paper		90	
2. Whatman	GF/A	Glass	Determination of suspended solids in water and effluents	90	1.6
3. GelmanSciences	A/E	Glass fibre	For dissolved and suspended solids in water and gravimetric analysis of air pollutants	90	1
4. GelmanSciences	Metricel GA-4	Hydrophilic polypropylene		47	0.8
5. Whatman	GF/F	Glass	Used in the TCLP-test of EPA	90	0.7
6. GelmanSciences	Metrigart™	Glass		47	0.5
7. Schleicher & Schuell	NC 50/20	Cellulose nitrate	Sterility testing, microorganism detection	50	0.45
8. Schleicher & Schuell	OE 67	Cellulose acetate	Scintillation and residue analysis	100	0.45
9. Schleicher & Schuell	ME 25/20	Cellulose ester	Filter-off analysis, sludge investigation, coliform bacteria analysis, total bacteria count, calometric determination, recovery of undissolved matter, silt density index, colloid index, micro quality control	50	0.45
10. Schleicher & Schuell	NL 17	Polyamide	Sterilising filtrations, HPLC sample preparation	142	0.45
11. GelmanSciences	Nylaflo®	Hydrophilic nylon		90	0.45
12. GelmanSciences	Nylaflo®	Hydrophilic nylon		47	0.45
13. GelmanSciences	Supor®-450	Hydrophilic polyethersulfone	For biological, pharmaceutical filtration requirements	90	0.45

The effect of different environmental parameters on leaching was or will be studied using batch shaking tests for the following test conditions:

Parameter	**Testing conditions**
Eluate: pH	- 4,6,8,10
Shaking time and pH	- 1 d, 2 d and 7 d at 2 different pH-values
L/S-ratio	- 2, 10
Temperature	- 4 ° (to be done) and 20 °C

In the selection of test arrangements suitable for organic contaminant leaching testing the following items were to be defined:

- Assessment of filter sorption
- Selection of filtration technique
- Arrangements in pH static leaching test
- Arrangements in column testing (filters, contact time)

3. RESULTS AND DISCUSSION

3.1 Influence of membranes on the concentrations in the eluates

3.1.1 PCBs

Influence of membrane types (pore size) and sorption of PCBs on filters were studied using batch leaching tests with one leaching step at L/S 10. Two soil samples, a natural contaminated humus rich soil with 30 ppm of PCBs and a spiked humus rich soil sample containing about 60 ppm PCBs were used. The test results on filter sorption for PCB-contaminated soil samples are shown in Tables 3 and 4. Based on the results the following conclusions can be drawn:

- The filtration times for the leachates from the real contaminated soil were almost identical which indicates no differences in clogging of filters (no influence of soil residue upon the filters). The influence of sorption was identical or insignificant between the tested filters.
- The filtration times for the leachates from spiked samples were significant longer than for the real sample. The PCB concentrations in the eluates from the spiked sample were clearly dependent on the pore size of membranes. The centrifugated sample contained the highest amounts of PCBs. Coarse membranes with pore size over 1 μm resulted in higher eluate concentrations indicating particle bound leaching. The difference in results from membranes with pore size less than 1 μm was not significant.
- Use of cellulose nitrate membranes gave in this test series the lowest concentrations which might be due to sorption on the membrane.
- For recommendation of suitable filter membranes further studies are needed, e.g. testing of coarser membranes in comparison to centrifugation. Also a discussion on the maximum particle size in the eluate is needed.

Table 3.
Leaching from a real PCB-contaminated soil sample (30 000 μg/kg) in preliminary batch shaking tests with four different filter types (vacuum filtration, filter diameter 90 mm).

Mem bran no	**Membran material**	**Filter diameter (mm)**	**Pore size (μm)**	**Filtration time**	**Leached amount μg/kg (IUPAC-number)**						**Total PCBs**
					52	**101**	**118**	**138**	**153**	**180**	
1.	Paper	90	Not specified		0.04	0.46	0.14	0.89	0.41	0.19	**5.8**
5.	Glass fibre	90	0.7	1:10	0.07	0.45	0.14	1.1	0.40	0.16	**6.1**
11.	Hydrophilic nylon	90	0.45	1:07	0.04	0.49	0.15	0.94	0.24	0.10	**5.3**
13.	Hydrophilic polyethersulfone	90	0,45	1:01	0.03	0.49	0.18	0.87	0.25	0.11	**5.2**

Table 4.
Leaching from a spiked PCB-contaminated soil sample (60 000 µg/kg) in preliminary batch shaking tests with six different filter types (vacuum filtration).

Membran no	Filter material	Filter diameter (mm)	Pore size (µm)	Filtration time (h:min)	pH of eluate	Leached amount, ug/kg IUPAC-number						Total PCBs
						52	101	118	138	153	180	
-	Centrifugation			-	6.8	2.6	27	<0.1	63	57	80	620
1.	Paper	90	Not specified	9:37	5.9	0.8	6.9	1.6	24	18	35	240
2.	Glass	90	1.6	2:27	6.8	0.9	3.9	0.7	9.6	7.3	12	94
2.	Glass	90	1.6	2:11	6.2	1.0	7.4	1.3	20	17	25	190
2.	Glass	90	1.6	2:38	6.6	1.8	15	2.7	45	38	61	440
3.	Glass	90	1	2:04	6.7	1.0	5.9	1.1	17	12	22	160
4.	Hydrophilic polypropylene	47	0.8		6.6	0.2	0.4	0.1	0.5	0.5	0.3	5.2
5.	Glass	90	0.7	2:27	6.8	0.9	3.1	0.5	5.8	4.7	6.3	58
5.	Glass	90	0.7	2:33	6.7	0.9	3.9	0.5	6.0	5.7	7.0	65
5.	Glass	90	0.7	2:02	7.1	1.3	5.2	0.6	8.6	7.2	8.1	84
7.	Cellulose nitrate	50	0.45		6.5	0.1	0.2	<0.1	0.5	0.5	0.8	5.5
6.	Glass	47	0.5	9:32	6.5	0.3	2.0	0.5	7.4	6.7	13	82
9.	Cellulose ester	47	0.45		6.4	0.2	0.5	0.2	0.5	0.5	0.5	63

3.1.2 Chlorophenols

The test results on filter sorption for Chlorophenol contaminated soil samples are shown in Tables 5-7. The following conclusions can be drawn:

- Only small differences between filters were observed. The eluates from tests with the paper filter and the glass fibre filters (GF/A,GF/F, Metrigard) showed the highest concentrations of chlorophenols. The filtration technique (pressure contra vacuum) had in this case no clear influence on the results.
- The differences in filtration times were significant (1-8 hours) indicating clogging of the filters. In some cases this might be explained by the differences in filter size (resulting in a variation of the thickness of soil layer on the filters acting as an extra filter)
- The results for particle size analysis of some eluates indicate that the particle bound leaching was small. In the case of humus soil, new big particles were formed after filtration during the storage of sample for the particle size analysis.
- The choice of membranes can be done upon practical reasons: availability and price of membranes and practicability in the laboratory work (size, filtration time).

Table 5.
Leaching from Chlorophenol contaminated soil (3 000 µg/kg) in preliminary batch shaking tests with different filter types.

Mem bran no	Filter material	Filter diameter (mm)	Pore size (µm)	Filtration technique	Filtration time (h)	Leachate pH	Leached amount of 2,3,4,6-tetrachloro-phenol (µg/kg)	Leached amount of pentachloro-phenol (µg/kg)
1	Paper	90		Vacuum	4:59	6.2	<3	2.7
5	Glass	90	0.8	Pressure	1:15	6.9	3.7	4.8
6	Glass	47	0.5	Vacuum	7:05	6.8	2.9	4.0
7	Cellulose nitrate	50	0.45	Vacuum	5:58	7.1	2.5	3.2
7	Cellulose nitrate	50	0.45	Vacuum	7:39	6.6	<3	2.7
8	Cellulose acetate	100	0.45	Vacuum	0:59	5.8	<3	<3
8	Cellulose acetate	100	0.45	Vacuum	1:15	6.6	<3	<3
9	Cellulose ester	47	0.45	Vacuum	3:59	7.4	<3	3.2
10	Polyamide	90	0.45	Pressure	5:41	6.7	<3	<3
11	Hydrophilic nylon	90	0.45	Vacuum	1:30	6.5	<3	<3
13	Hydrophilic polyethersulfone	90	0.45	Vacuum	1:11	6.5	<3	<3
13	Hydrophilic polyethersulfone	90	0.45	Vacuum	1:39	6.8	<3	<3
13	Hydrophilic polyethersulfone	90	0.45	Pressure	0:54	6.0	<3	<3

Table 6.

PCP-concentration 120 mg/kg. Humus rich soil. L/S 10.

Membran no + Membran material	Filter diameter (mm)	Pore size (µm)	Particle size distribution µm, cumulative %												Filtration time (h)	pH of eluate	Leached amount of Chlorophenols, mg/kg			
			0.29	0.36	0.44	0.55	0.68	0.84	1.0	1.3	1.6	2.0	2.4	3.0			2,4,6-	2,3,4,6	Penta	Total
Sedimentation			0	0	0	4	16	**38**	**61**	**74**	**75**	**78**	**97**	97	-	6.1	1.8	0.45	0.78	3.0
Sedimentation			2	9	22	40	59	**73**	**80**	**82**	**82**	**87**	**99**	99	-	6.5	1.8	0.43	0.75	3.0
Centrifugation			0	23	42	42	42	42	42	42	42	42	100	100	-	6.4	1.4	0.36	0.46	2.2
Centrifugation			0	9	34	62	74	74	74	74	74	74	101	101	-	6.4	1.7	0.46	0.61	2.8
2. Glass	90	1.6	0	0	0	0	9	**36**	**72**	**94**	**94**	94	100	100	1:47	5.6	2.0	0.49	0.82	3.3
3. Glass	90	1	0	0	0	0	5	49	99	99	99	99	99	99	2:04	5.7	1.9	0.44	0.80	3.1
4. Hydrophilic PP	47	0.8	0	0	0	0	0	0	6	**51**	**100**	100	100	100	4:17	5.6	1.3	0.25	0.34	1.9
5. Glass			0	0	0	3	15	36	**56**	**66**	**66**	**73**	**99**	99	1:48	5.7	1.8	0.43	0.70	2.9
6. Glass	47	0.5	0	0	0	2	21	49	66	66	66	66	99	99	>	7.4	1.7	0.35	0.69	2.7
Pre-filtration 2 + 6 (see above)			0	0	0	0	7	**27**	**58**	**87**	101	101	101	101	1:54	5.7	1.6	0.31	0.48	2.4

Table 7.

PCP-concentration 90 mg/kg. Sandy soil. L/S 10.

Membran no + Membran material	Filter diameter (mm)	Pore size (µm)	Particle size distribution µm, cumulative %												Filtration time (h)	pH of eluate	Leached amount of Chlorophenols (mg/kg)			
			0.29	0.36	0.44	0.55	0.68	0.84	1.0	1.3	1.6	2.0	2.4	3.0			2,4,6	2,3,4,6	Penta	Total
Centrifugation			31	31	31	31	31	31	31	31	31	31	31	31	-	6.6	24	17	29	69
Centrifugation			48	48	48	48	48	48	48	48	48	48	48	48	-	6.6	25	17	29	70
Sedimentation			100	100	100	100	100	100	100	100	100	100	100	100	-	6.3	30	15	34	79
Sedimentation			100	100	100	100	100	100	100	100	100	100	100	100	-	6.3	32	17	35	84
1. Paper	90		7	47	95	100	100	100	100	100	100	100	100	100	2:35	6.1	31	17	45	93
2. Glass	90	1.6													1:25	6.5	37	15	37	89
3. Glass	90	1													1:03	6.8	40	16	36	92
4. Hydrophilic PP	47	0.8	0	9	52	96	100	100	100	100	100	100	100	100	3:41	6.4	26	15	35	76
5. Glass	90	0.8													1:02	6.6	37	16	41	94
6. Glass	47	0.5													1:37	6.7	40	15	41	96
6. Glass	47	0.5	0	92	100	100	100	100	100	100	100	100	100	100	4:29	6.7	28	14	31	73
7. Cellulose nitrate	47	0.45													3:12	6.5	37	15	34	86
8. Cellulose acetate	100	0.45													2:15	6.4	22	7.3	24	53
9. Cellulose ester	47	0.45													3:08	6.5	34	15	36	85
10. Polyamide	90	0.45													3:14	6.4	32	11	11	54
11. Hydrophilic nylon	90	0.45													1:21	6.6	14	2.5	1.7	18
12. Hydrophilic nylon	47	0.45													7:12	6.5	26	13	22	61
13. Hydrophilic polyether sulfone	90	0.45													2:05	6.6	30	12	28	70
Prefiltration 2. + 6 (see above)			89	89	89	89	89	89	89	89	89	89	89	89	2:16	7.0	30	16	32	78

3.2. Batch leaching test with chlorophenol contaminated soils

Leaching tests with one or two leaching steps were performed with different contact times (see Table 8). The following conclusions can be drawn:

- The leachability from sandy soil was high, indicating no sorption to the soil matrix or the membranes.
- The leachability from humus soil was significantly lower due to sorption to humus.
- The contact time in the batch leaching tests had little effect on the leachability.
- No significant difference can be seen between the one or two step leaching at L/S 10.
- A long contact time (7 d) in the leaching test caused a long filtration time probably due to formation of small particles which clogged the membranes. The long contact time had no significant influence on the leached amount.

Table 8.
Batch leaching tests with one or two leaching steps with different contact times.

	L/S 2							Cumulative L/S 10						
Soil type + Concentration	**Contact time**	**Filtration time**	**pH**	**Leached amount of Chlorophenols (mg/kg)**				**Contact time**	**Filtration time**	**pH**	**Leached amount of Chlorophenols (mg/kg)**			
				2,4,6	**2,3,4,6**	**Penta**	**Total**				**2,4,6**	**2,3,4,6**	**Penta**	**Total**
Sandy soil : 90 ppm	6 h	0:09	6.6	10.8	6	9.2	26	18 h	0:09	6.5	21	15	30	66
	48 h	1:17	7.1	9	4.8	6.6	10.4	18 h	4:34	7.2	19	14	24	57
	48 h	4:41	7.1	8.8	4	5.4	18.2	18 h	-	-	-	-	-	-
	***)	-	-	-	-	-	-	1 d	2:16	7.0	30	16	32	78
	***)	-	-	-	-	-	-	1 d	*)	6.6	24	17	29	69
	***)	-	-	-	-	-	-	1 d	*)	6.6	25	17	29	70
Humus rich soil: 120 ppm	***)	-	-	-	-	-	-	7 d	-*)	5.9	1.8	0.77	1.3	3.9
	***)	-	-	-	-	-	-	7 d	-*)	5.9	1.8	0..8	1.4	4.0
	***)	-	-	-	-	-	-	2 d	2:54	6.0	1.8	0.59	0.81	3.2
	***)	-	-	-	-	-	-	2 d	2:55	6.1	1.7	0.55	0.78	3.0
	***)	-	-	-	-	-	-	2 d	-	5.6	1.5	0.6	1.0	3.1
	***)	-	-	-	-	-	-	1 d	*)	6.4	1.4	0.36	0.46	2.2
	***)	-	-	-	-	-	-	1 d	*)	6.4	1.7	0.46	0.61	2.8
	***)	-	-	-	-	-	-	1 d	1:54	5.7	1.6	0.31	0.48	2.4
Humus rich soil: 1400 ppm	6 h	0:17	5.0	4.4	1.1	1.1	6.5		>7	5.5	19	5	6	31
	48 h	2:17	5.7	<0.01	0.002	3.4	3.4		2:38	5.6	-	-	-	-
	48 h	0:37	5.6	0.01	0.9	6.7	7.6		5:57	6.0	0.08	15	51	66
	***)	-	-	-	-	-	-	1 d	3:45	5.3	14	4.8	5.5	24
	***)	-	-	-	-	-	-	1 d	3:44	5.3	20	6.2	7.7	33
	***)	-	-	-	-	-	-	7 d	7:53	5.9	9.5	4.6	6.1	20
	***)	-	-	-	-	-	-	7 d	7:50	5.8	18	5.9	8	32
	***)	-	-	-	-	-	-	2 d	2:40	5.9	13	5	6.2	24
	***)	-	-	-	-	-	-	2 d	2:38	5.8	17	6.1	8	31
	***)	-	-	-	-	-	-	2 d	2:16	5.9	19	6.2	8.2	33
	***)	-	-	-	-	-	-	2 d	2:14	5.9	19	6.3	8.2	34

*) Centrifugation. **) magnetic bar agitation . ***) only one step leaching at L/S 10

3.3 Influence of pH on the leaching from chlorophenol contaminated soils

The influence of the pH was studied at a few pH values. The conclusions are following:

- The leachability increased at pH 8 compared to pH 5-6
- The leachability at pH 8 or pH 10 was near 100 %.
- A contact time of 2 days, which has been discussed generally for the pH static test, is sufficient for the leaching of chlorophenols.

Table 9.
Results from the pH static tests with humus rich soil with two contamination levels.

Target pH	**Contact time**	**Acid/base consumption mol H^+/kg**	**2.4.6-**	**2.3.4.6-**	**Penta**	**Total**
		Humus rich soil 120 mg/kg				
4	2 d	0.19	1.3	0.3	0.2	1.8
5 own	2 d	-	1.5	0.6	1.0	3.1
6	2 d	0.09	<0.1	1.4	5.7	7.0
8	2 d	0.54	33	22	27	82
8	2 d	0.55	32	22	30	85
8	7 d	0.51	34	31	50	116
10	1 d	1.37	-	-	-	-
10	2 d	1.33	34	25	39	99
10	2 d	1.41	35	26	39	100
10	7 d	1.73	41	39	71	150
		Humus rich soil 1400 mg/kg				
5.1 (own)	2 d	-	16	7	11	34
6	2 d		<1	83	614	697
8	2 d		310	240	390	940
8	7 d	0.56	340	250	350	940
10	2 d	1.18	370	280	460	1110
10	7 d	1.61	400	290	430	1120

NA = not analysed

3.4 Repeatability of tests

The repeatibility is affected by the test performance (test conditions. sample preparation) and the chemical analysis of the eluate. The uncertainity in the chemical analysis was estimated to be around ± 30 %.

Some replicates were done in the membrane testing for leaching of PCBs (see the results for replicates for membranes 2 and 5 in Table 4). The differences in results are significant indicating need for further studies on the repeatability of the tests.

Leaching studies of chlorophenols has been performed with replicates (see Tables 8 and 9). Because the sorption effect on the membranes was estimated to be small, also the results for membrane testing can be interpretated as replicates (see Tables 6 and 7). Especially the replicate studies in the pH static test with defined testing conditions were good. The risk for sorption onto filters and equipment is low for chlorophenols, probably due to the high water solubility. In this case the most uncertainity arises from the chemical analysis.

3.5 Preliminary conclusions of the leaching behaviour

3.5.1 PCB

The following conclusions on the leaching behaviour of PCB can be drawn from Tables 3 and 4:

- The composition of PCB-congeners in the eluate is probably dependent on the origin of the soil sample. The eluate of the real sample contained higher concentrations of PCB congener 138 than other analysed congeners.
- The concentrations in the eluates were generally low. Especially the eluate from the real soil sample contained low concentrations of PCBs. This was also to be expected due to the low leachability of PCB and the humic nature of the samples. The eluate from the spiked soil sample contained, however, several times higher concentrations of PCBs than the corresponding eluate of the real soil sample. This indicates some effect of aging in the soil samples.

3.5.2 Chlorophenols

The following conclusions on the leaching behaviour of chlorophenols can be drawn:

- The concentrations of chlorophenols in eluate were low from the real contaminated soils indicating that the leachable fractions had already been washed out from the soil.
- The leachability of chlorophenols was very high from the sandy soils indicating very little sorption to the soil matrix. The influence of the soil matrix was significant for the humus soils.
- No particle bound leaching of chlorophenols could be seen.
- The results explain the difficulties in finding suitable real sample from contaminated saw mill sites. The contaminated soil layers at the contaminated saw mill sites were usually wood chips. Only small concentrations could be found in clay soils indicating the transport of leached chlorophenols into the environment.
- The leaching rate from soil to water phase is quick. A contact time of 1-2 days in the tests was sufficient.
- The leachability increases at higher pH-values. The main part of chlorophenols were leached out at pH 8.

4. FUTURE TASKS

The experimental program for studies on the factors controlling the leaching process will be continued with column tests and batch leaching tests (e.g. pH static tests). In the case of PCB. a discussion is needed on the separation technique for eluate in the tests. The concentration in eluates is strongly influenced by the separation system (centrifugation contra membrane filtration). If possible, real samples will be tested with a short test program and the results will be compared to the spiked samples.

The results for chlorophenols and PCB will be compared to the leaching results obtained for PAH in the EU-project. The aim is to have similar approach in the leaching studies for PAHs. PCBs and chlorophenols.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Forecasting the long-term behaviour of municipal solid waste incineration bottom ash: rapid combined tests

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Municipal solid waste incineration bottom ash is a highly reactive material, especially toward atmospheric CO_2, which is why we decided to carry out rapid and simple tests combining accelerated ageing and batch leaching to forecast the long-term behaviour of bottom-ash samples of various origins. By speeding up one of the major reactions, i.e. the carbonation that occurs during the natural maturation of bottom ash, it was possible to determine the maximum pollutant release of the elements (metals, sulphates) most detrimental to upgrading. The final products present higher calcite contents and are characterized by a reduction in leachate metals and an increase in leachate sulphates. The laboratory results are in agreement with a full-scale field study carried out elsewhere. Thermodynamic calculations were also undertaken to determine the cause of the high exothermicity evidenced during the tests because, even though the oxidation of metals (Fe, Al) is mainly invoked to explain the general increase of bottom-ash temperature during maturation, the contribution of the carbonation reactions (with portlandite, wairakite, larnite anorthite) cannot be ignored.

1. INTRODUCTION

Most waste produced by thermal processes is highly reactive at ambient temperature, and this is particularly so for municipal solid waste (MSW) incineration bottom ash. During maturation, this waste undergoes significant changes that alter the chemical nature of its leachates.

Studies carried out on the chemical stability of bottom ash subjected to chemical weathering have, in particular, shown an improvement in leachate quality for soluble salts and metals (Pb, Zn, etc.). Conversely, sulphates are more likely to be released. These conflicting trends are essentially linked to a) the mobility of salts and b) the carbonation process that stabilizes the metals and increases sulphate solubility [1,2].

At present, French legislation relies on a batch leaching test (NF X31-210) to evaluate the release potential for a number of elements (SO_4, Pb, Cd, CrVI, As, Hg, TOC). However, this prescriptive test only accounts for element release at the time of the measurement. It is therefore inadequate for estimating the long-term behaviour of materials likely to evolve over time.

Tests combining accelerated ageing and batch leaching have been developed using the results of a full-scale study. These enable a rapid estimation of the maximum release values for carbonation-aged bottom ash. The study specifically monitored the elements most detrimental to upgrading (Pb, SO_4).

2. MATERIALS AND METHOD

2.1. Samples and mechanical preparation

The experiments were performed on five samples of bottom ash of various origins, both freshly produced (F1, F2, F3) and stored (S1 [stored for more than five years] and S2 [stored for two years]).

The samples, some 30 kg each, were first dried at 80-100 °C before magnetically removing any iron particles. Ash particles larger than 4 mm diameter were then reduced to 4 mm and mixed into the <4 mm fraction in a cement mixer. During this mixing, water was progressively sprayed through the bottom ash for a period of 15 minutes so as to obtain a constant water content of 5% w/w in all the samples; this is deliberately well below the initial water content of around 15-20% in order to reduce the kinetics of the carbonation process. The samples were then successively quartered in order to obtain representative and relatively homogenous 1.5 kg splits.

2.2. Ageing tests

Five plexiglass percolation columns (one for each bottom ash) connected in series with a CO_2 bottle were used for the ageing tests. Each column was equipped with a valve at each end, and a 'scatter system' was placed at the bottom to improve the CO_2 diffusion during upflow. A manometer was attached to each column to measure the internal pressure.

Around 1.5 kg of bottom ash was placed in each column. After air flushing, the samples were subjected to a slight overpressure of CO_2 gas upflow for increasing periods of time (20 min, 40 min, 1 h, 3 h, 6 h). At the end of the experiment the samples were dried at 80-100 °C.

As the reaction appeared to be highly exothermic, the temperature variations of the 6-hour experiment were recorded during the accelerated ageing of the three samples of freshly produced bottom ash (F1, F2, F3).

2.3. Leaching tests/leachate analysis

As described in the French standard batch leaching test (NF X31-210), the dry equivalent quantity of a 100 g wet sample reduced to 4 mm is mixed with water to a liquid/solid ratio of 10 and agitated for 24 h.

A simplified and arbitrary procedure of mixing 90 g dry solid with 1 litre of water was used for the present leaching tests on both the untreated and CO_2-treated samples. The leachates were then filtered at 0.45 µm and, after measurement of their pH, analysed for lead and sulphate content by ICP and ion-exchange chromatography, respectively.

2.4. Infrared spectroscopy

Infrared spectroscopy was used to verify that the carbonation process had taken place in the bottom ash. KBr pellets were prepared for both the non-carbonated sample and the 6-hour aged samples (maximum treatment). Special care was taken to obtain representative subsamples by successive quartering, then crushing to 80 μm and grinding to lower granulometry.

3. RESULTS

3.1. Monitoring the CO_2 treatment

The upflow of CO_2 in the columns containing the freshly produced bottom ash (F1, F2, F3) showed that the bottom-ash reactivity towards carbonation is exothermic, with an initial rapid heating (Fig. 1a). The same pattern was noted with the two-year-old stored bottom ash S2. The stored bottom ash S1 (more than five years old), however, showed no evidence of temperature variation throughout the 6-hour treatment.

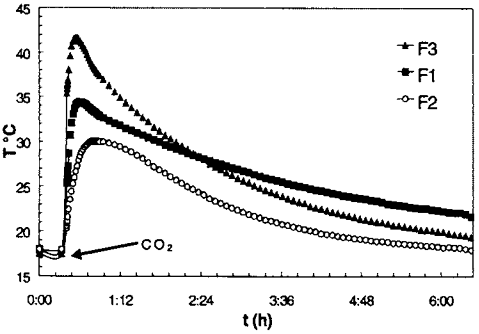

Figure 1a. Temperature profile of the freshly produced bottom ash (F1, F2, F3) during the CO_2 treatment.

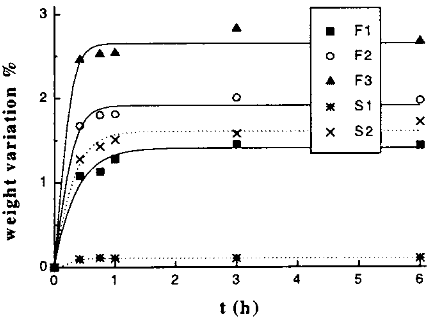

Figure 1b. Weight variation of the five bottom ash samples during the CO_2 treatment.

The bottom ash reactivity towards CO_2 also resulted in a rapid weight variation for F1, F2, F3 and S2, the maximum being reached after about one hour, whereas once again no significant change was noted for S1 (Fig. 1b).

3.2. SO_4 and Pb leaching behaviour

As expected from the full-scale study results, sulphate leaching increased with the accelerated CO_2 treatment. Apart from S1, a sulphate release plateau was identified after a few minutes of carbonation in the bottom ash leachates (Fig. 2a).

This reaction was accompanied by a decrease in the pH values (Fig. 2b). The fresh bottom-ash (F1, F2, F3) leachates, initially at around pH 11.5-13.0, fell to pH 9.0-9.5 after ageing. The change in pH of the leachates from the stored bottom ash (S1, S2) was significantly less: from pH 10 to pH 8.5 for S2, and no significant variation for S1 (steady at pH 8.0-8.5).

The leachates of the non-carbonated F2 and F3 bottom ash also contained 0.57 and 4.87 mg/kg of Pb, respectively. The Pb concentrations for all the other samples (both non-carbonated and carbonated) were below the detection limit (0.02 mg/kg).

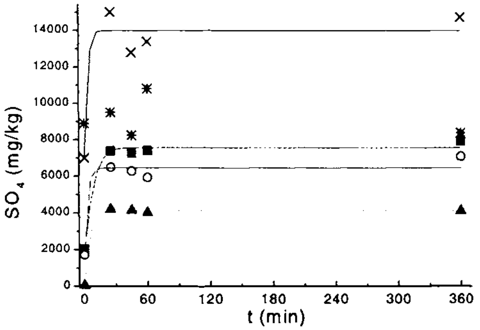

Figure 2a. SO_4 release in the leachates of the five bottom ash samples during CO_2-accelerated ageing with time.

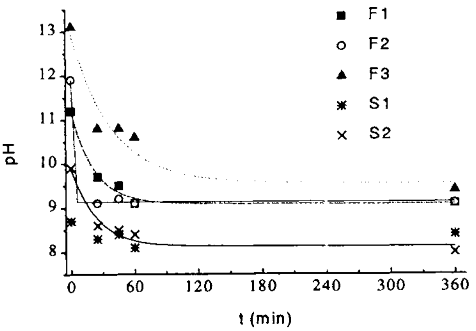

Figure 2b. pH evolution of the leachates.

3.3. Solids description

The Fourier transform infrared (FTIR) spectra of the bottom ash samples both before and after carbonation made it possible to monitor the chemical evolution of the solids content during the treatment. This was especially significant for the two extreme cases, i.e. the F3 fresh bottom ash, which showed the highest temperature rise (up to 42 °C), and the S1 stored bottom ash, which showed no significant change during carbonation.

Before accelerated ageing, the F3 bottom ash spectrum showed the main characteristic peaks of calcite (1430, 875 and 713 cm^{-1}) and a small peak at 3645 cm^{-1} corresponding to the OH vibration band of portlandite. After the 6-hour treatment the portlandite peak disappeared and a higher calcite content is detected (Fig. 3a).

The spectra of S1 bottom ash before and after treatment are superimposable, in agreement with no reactivity towards CO_2. The portlandite peak is absent and the peaks relative to the presence of calcite are identical (Fig. 3b). Calibration from ternary mixtures (decarbonated bottom ash / portlandite / calcite) is consistent with a 2-5% portlandite content in the F3 bottom ash.

For the intermediate samples (F1, F2, S2) the portlandite peak was not distinguished on either the treated or untreated sample spectra. Nevertheless, the samples contained a higher calcite content after treatment than before (as shown by the increased intensity of the three main characteristic peaks). Thus if portlandite is present in these samples, its content is necessarily below 1-2%. Minerals other than portlandite (non detectable by FTIR) may also be carbonated.

Even if complementary calibrations and special bottom ash preparation (for example fine particle separation) were to be developed, infrared spectroscopy still appears to be an efficient tool for determining the maturation state of bottom ash and its evolution during carbonation.

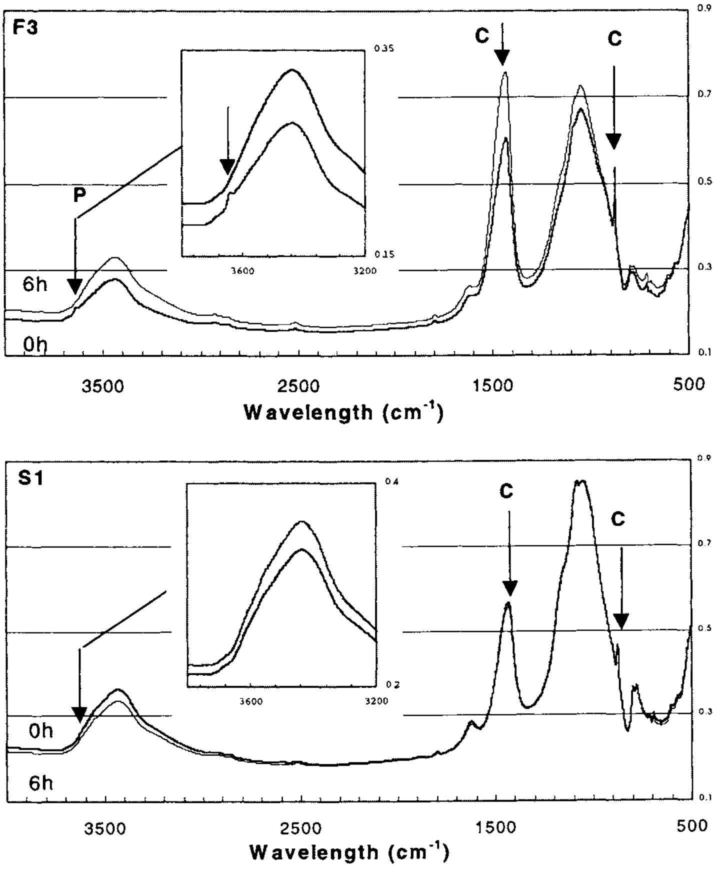

Figure 3. FTIR spectra of freshly produced (F3) and stored (S1) bottom ash before (0 h) and after (6 h) CO_2 treatment (c: calcite; p: portlandite).

4. INTERPRETATION/DISCUSSION

Apart from sample S1 (bottom ash stored for more than five years), the tested samples of MSW incineration bottom ash all showed a similar evolution during the combined tests. In particular, maximum sulphate release from the leachate was attained in less than 1 h of treatment with CO_2 gas. The results also showed that contained lead was trapped during the carbonation treatment.

Sample S1 did not react to the accelerated carbonation. Moreover, the pH of its leachate was constant at around 8, which signifies that it had already attained peak maturation during its storage.

The initial quantities of leached Pb and SO_4 obviously depend on the nature, and thus the origin, of the bottom ash. The sulphate content of sample S2 was higher than that of sample F1, which in turn was higher than that of F2, again higher than that of F3. During the accelerated maturation, the quantity of released sulphates was multiplied by a factor of 2 for sample S2 (already naturally aged over two years), by a factor of 4 for samples F1 and F2, and by a factor of 84 for sample F3. The last, which gave the most basic leachates (pH 13) corresponds to the 'youngest' of the fresh bottom waste samples.

Table 1.
Enthalpy of the carbonation reactions of certain calcic minerals in bottom ash and of the oxidation of iron metal (Fe(s)) and aluminium metal (Al(s)).

Mineral	**Reaction**	**log K (25°C)**	**ΔH_R (kcal)**	**ΔH_R pH=13.46**	**ΔH_R pH=12.23**
Portlandite	$Ca(OH)_2(s) + CO_2(aq) \Leftrightarrow$ Calcite + H_2O	14.20	-22.10	-10.91	-14.05
Ettringite*	0.33 Ett. + $CO_2(aq) \Leftrightarrow$ Calcite + Gypsum + 0.33 Al_2O_3 + 8.67 H_2O	10.08	-0.85	16.51	13.40
Wairakite	$Ca(Al_2Si_4)O_{12}{:}2H_2O + CO_2(aq) \Leftrightarrow$ Calcite + + Kaolinite* + 2 Chalcedony	10.53	-27.10	-9.05	-12.20
Prehnite	0.5 $Ca_2Al_2Si_3O_{10}(OH)_2$ + $CO_2(aq)$ + 0.5 H_2O $\Leftrightarrow$ Calcite + 0.5 Chalcedony + 0.5 Kaolinite*	6.73	-14.42	3.65	0.50
Diopside	$CaMgSi_2O_6 + CO_2(aq) + H_2O \Leftrightarrow$ Calcite + 2 Chalcedony + Brucite	3.93	-11.91	6.17	3.01
Anhydrite	$CaSO_4 + CO_3^{-2} \Leftrightarrow$ Calcite + SO_4^{-2}	4.17	-1.81	-1.65	-1.39
Larnite	0.5 $Ca_2SiO_4 + CO_2(aq) \Leftrightarrow$ Calcite + 0.5 Chalcedony	12.95	-22.42	-4.46	-7.61
Anorthite	$Ca(Al_2Si_2)O_8 + CO_2(aq) + 2\,H_2O \Leftrightarrow$ Calcite + Kaolinite*	11.58	-27.67	-9.60	-12.76
Fe(s)	1.333 $Fe(s) + O_2(aq) \Leftrightarrow$ 0.667 $Fe_2O_3(s)$	121.49	-175.36	-125.31	-111.41
Al(s)	1.333 $Al(s) + O_2(aq) + 2\,H_2O \Leftrightarrow$ 1.333 $Al(OH)_3(s)$	189.64	-274.45	-237.19	-223.29
Pyrite	0.211 $FeS_2(s) + O_2(aq)$ + 0.737 $H_2O \Leftrightarrow$ 0.211 $Fe(OH)_3(s)$ + 0.421 SO_4^{2-} + 0.482 H^+	47.03	-71.17	-47.45	-32.11
Pyrrhotite	0.444 $FeS(s) + O_2(aq)$ + 1.111 $H_2O \Leftrightarrow$ 0.444 $Fe(OH)_3(s)$ + 0.444 SO_4^{2-} + 0.889 H^+	61.03	-94.49	-68.69	-53.28

The ΔH_R (kcal) values are given for 25 °C under standard conditions. ΔH_R (pH = 13.46) corresponds to the enthalpy of the reaction in a bottom waste leachate (I = 0.47, log fCO_2 = -11.78, log fO_2 = -29.28, log $aCO_2(aq)$ = -13.29, log $aO_2(aq)$ = -32.22), and ΔH_R(pH = 12.23) is calculated for a less saline leachate (I = 0.19, log $fCO_2(g)$ = -9.47, log $fO_2(g)$ = -39.46, log $aCO_2(aq)$ = -10.94, log $aO_2(aq)$ = -42.36).

*Detailed chemical formula: Ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}26H_2O$; Kaolinite $Al_2Si_2O_5(OH)_4$.

The results of the laboratory study reflect the observations of a full-scale study made in the field on the alteration mechanisms of a large bottom ash heap subjected to atmospheric weathering and where CO_2 consumption was evidenced and calcite found to be the predominant neoform mineral generated. A 22-month monitoring of species concentrations in the leachates indicated three major stages in the maturation process: 1) chloride leaching, 2) carbonation with Pb, Zn trapping, and 3) late sulphate leaching [1,2]. Meima and Comans (1999) came to similar conclusions in a separate study [3].

The temperature increase noted in the columns during the accelerated tests is unmistakably linked to the carbonation of highly reactive phases and notably to the presence of portlandite. This carbonation reaction also probably plays a role in the temperature rise noted during the natural maturation of bottom waste, despite the fact that the reactions generally quoted in the literature to explain this rise correspond to the oxidation of the metals Fe°, Al° [4]. At this stage of the study, therefore, we considered it essential to determine the relative importance of the carbonation reaction in the exothermic stage undergone by all bottom ash on a maturation site.

Because of the variety of mineral species present in MSW incineration bottom ash, numerous reactions, such as carbonation, oxidation-reduction and hydration, are likely to influence the maturation (Table 1). The minerals that we have taken into consideration are typical minerals found in MSW incineration bottom ash (portlandite, ettringite, larnite, anhydrite), minerals associated with zeolites (wairakite, prehnite) present in the first stages of ageing, high-temperature minerals derived from melts (diopside, anorthite), metals that are always present at the end of combustion (Al°, Fe°), and sulphides (pyrrhotite, pyrite). More than 40 reactions were calculated. As a first approximation, with regard to the aluminium oxides, the reaction product has been defined as close to Al_2O_3 even where present as $Al_2O_3.nH_2O$ gels [5].

Under standard conditions, all the reactions are theoretically exothermic ($\Delta H°R<0$) as shown by the calculations made using the SUPCRT92 software [6].

If one considers the effect of salinity on ion activity (calculations done with the EQ3NR software [7]) it is seen that in fact only a few reactions are likely to be sufficiently efficient to explain the temperature rise. The remaining possibilities are i) the carbonation of portlandite, larnite and anhydrite, ii) the carbonation of anorthite and wairakite accompanied by the formation of kaolinite, iii) oxidation of the metals, and iv) hydrolysis of the sulphides. Of these, the last two are the most exothermic. The carbonation of calcium sulphates, such as ettringite, anhydrite and gypsum, is not an exothermic process.

Moreover, the reactions are highly dependent on the ionic strength. In general, reaction enthalpy increases by 1 kcal per gram of salinity, and if salinity is too high it can inhibit the reactions.

In bottom waste from which iron particles have been magnetically removed, the mass percentages of native metals are of the order of 3% for Fe° and 0.5% for Al°, with sulphides about 0.5% and portlandite about 6%. The amount of freeable energy is associated mainly with oxidation reactions of the metals and of some sulphides, rather than with the carbonation reaction.

However, this observation must be modulated by parameters such as specific surface area of the minerals and/or size of the crystallites, which play a not insignificant role in the level of reactivity. All the observations show that the cited metals are present in forms with limited surface areas, initial manufactured goods (Fe°), melt drops (Al°) or globules (sulphides) commonly included in glass, unlike the portlandite that is present as fine crystallites highly accessible to the fluids. The high calorific potential of the metals and sulphides will thus be compensated by the specific surface area of the minerals susceptible to carbonation and each of the components will play a role in the temperature rise associated with the natural maturation of the bottom waste.

5. CONCLUSION

Conducting leaching tests on artificially-aged MSW incineration bottom ash is proving to be a valuable tool in forecasting its long-term behaviour, because the physico-chemical characteristics of the obtained leachates correspond to those of fully-matured bottom ash. Ageing can therefore be achieved in a few hours in the laboratory, as against months and even years, depending on storage conditions, for the natural ageing process.

Moreover, in cases where the threshold values of toxic elements in the bottom ash are exceeded, this test enables one to determine the most suitable treatment to upgrade the bottom ash on its leaving the incineration plant, such as improving its physico-chemical characteristics through the addition of mineral substances.

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Developments in electroremediation and phytoremediation for the treatment of metal contaminated soils

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This paper examines certain areas of progress in developing new methods of treatment for metal contaminated soils. Electroremediation, which involves the passage of low intensity direct current between suitably distributed electrodes, may be used either singly or in combination with other approaches for transporting and removing metal ions from soils of low permeability that are difficult to treat by conventional methods. Effective phytoremediation involving the use of metal accumulating plants depends on the selection of mutant types with specific genetic characteristics. A novel approach for the rapid isolation of appropriate strains of members of the genus *Brassica* is currently under investigation and is outlined in this paper.

1. INTRODUCTION

Conventional methods for the treatment of metal contaminated soils involve removal of topsoil to landfill sites, immobilisation of metals within the soil and cleaning soil off-site by, for example, washing or acid-leaching. These techniques are very expensive and either do not address the problem that the metals remain in the soil and so may leach out at a later date or result in considerable damage to the soil structure and ecology.

Some of the more novel methods of decontamination involve removal of metals in situ. One approach is the use of electroremediation, the passage of low intensity direct current through the soil to remove ionic contaminants dissolved in the pore water [1-3]. This is especially effective for low permeability soils which are difficult to treat by other methods. Removal of metals involves transport by means of ionic migration and, to a lesser extent, by means of electroosmosis of the pore water. Many experiments have been performed to demonstrate the transport and removal of heavy metals using electroremediation [4-9]. In general, these metals form ions which dissolve under the acidic conditions produced by formation of H^+ ions at the anode and under the alkaline conditions due to OH^- ion production at the cathode. However, the pH gradient which arises between the electrodes produces a region where the formation of metal hydroxides of low solubility results in their precipitation out of solution. Enhancement of metal removal involves techniques to dissolve or maintain the metal ions in solution so that transport to the electrodes can take place. Various reagents may be added either at the anode, e.g. a complexing agent like EDTA [10,11], or at the cathode, e.g. H^+ ions in the form of acetic acid [12]. Alternatively, simply washing the electrodes with water may lead to the removal of contaminating ions [1, 13,].

Potentially, one of the most effective applications of this technique is its use in combination with bioremediation. A successful example of the removal of organics by this approach is provided by the Lasagna Process [14, 15] in which electrodes are placed in the soil alternating with treatment zones containing bacteria capable of digesting the organic compounds. Application of a low intensity direct current causes flow of water and dissolved organics into the treatment zones where the organics are broken down into harmless substances.

A slightly different approach to the removal of heavy metal ions from soil is to combine electroremediation with phytoremediation, the use of plants to absorb and/or break down contaminants [16]. The application of a direct current to the soil at a metal-contaminated site would cause the metal ions to flow towards the surface making them available for metal-accumulating plants to absorb. This solves one of the problems of phytoremediation, viz. that plants can generally clean up only the surface layer of the soil. The advantages of phytoremediation include its low cost and its ability to decontaminate soil in situ with less damage than other techniques.

It has been known for some time that there are plants which accumulate considerably higher concentrations of certain metals compared with normal plants, regardless of the concentration of the metal ion in the soil. In 1977 the term hyperaccumulator was coined to describe these plants [17] (see table 1). A notable example of such a plant is provided by *Sebertia acuminata* which can have more than 20% of its dry weight as Ni [18]. It has been suggested that hyperaccumulators might be used to decontaminate soil [19] and field trials have been performed on the removal of metals such as Zn, Cd and Ni [20, 21, 22, 23, 24]. An interesting commercial application of using plants to take up metals from the soil is so-called phytomining where the plants are harvested and the metal extracted for economic benefit [19, 25]. The feasibility of this process has been shown by trials which have been carried out on the extraction of Ni, a relatively expensive metal [22, 23, 24].

Table 1
Metal ion concentrations (ppm) in dry weight of plants grown on metalliferous soil

Metal ion	Typical Concentration		Threshold concentration for hyperaccumulation
	Normal plant	Hyperaccumulator	
Cd^{2+}	2	100	100
Co^{2+}	3	5000	1000
Cr^{3+}			1000
Cu^{2+}	20	5000	1000
Mn^{2+}	1000	10000	10000
Ni^{2+}	20	5000	1000
Pb^{2+}			1000
Zn^{2+}	100	10000	10000

Values taken from (1) R.R. Brooks, in Plants that Hyperaccumulate Heavy Metals, CAB International, Wallingford, 1998, p. 64 and (2) A.J.M. Baker, S.P. McGrath, C.M.D. Sidoli & R.D. Reeves, Resources, Conservation and Recycling, 1994, 11, 41-49.

One of the problems with most hyperaccumulators is that, unlike crop plants, they have a low annual biomass. Thus, the overall yield may be low despite the high proportion by mass of metal uptake and, in consequence, the rate of decontamination too slow [see e.g. 20]. One possible solution is to increase biomass by addition of fertilisers [26] or growth hormones. This may, however, have other adverse effects on metal uptake. Alternative methods of improvement include the use of selective breeding or genetic manipulation techniques to produce plants with higher biomass and/or plants able to take up a range of metal ions.

Attempts have been made to identify crop or crop-related species which produce high biomass and also accumulate sufficiently high levels of heavy metals. There is some evidence that certain members of the Brassicaceae family, in particular the crop plant, *Brassica juncea* (Indian mustard), can accumulate high levels of Pb and other toxic metals [27].

A different approach is to find ways of enhancing uptake of metals in crop plants which produce a high biomass but are not hyperaccumulators. One method is to add metal chelating agents, such as EDTA, to the soil. This has been carried out for Pb, which is difficult to remove from contaminated ground because of strong binding to organic matter and soil minerals [16, 28, 29, 30]. Further increase in uptake can be generated by spraying phosphate fertiliser on the shoots to increase biomass or by applying a direct current to the soil to increase Pb^{2+} availability [16]. Recently, high uptake of Au has been induced in *Brassica juncea* and other plant species by the addition of ammonium thiocyanate to the growth medium [31].

Selective breeding and the use of genetic manipulation techniques provide further methods of producing plants with increased ability to dissolve and/or take up metal compounds. The technique of chemical mutagenesis has been used to produce a mutant of the pea plant which accumulates high levels of Fe and a number of other metals in its shoots [32, 33] and mutants of *Arabidopsis* which accumulate increased amounts of Pb [16, 34]. A different method has been used to produce an *Arabidopsis* plant which is tolerant to and can absorb Hg^{2+} ions and convert them to metallic Hg [35]. In this case, the ability to reduce Hg^{2+} ions has been conferred on the plant by transferring a bacterial gene to it. The possibility exists of making transgenic crop plants containing genes, which determine high uptake of metals, transferred from hyperaccumulators.

2. EXPERIMENTAL

In the work reported here, which is part of a feasibility study, we have initiated a selective breeding programme to produce high metal accumulator plants using rapid-cycling *Brassica rapa (syn. campestris)*, so-called `fast plants`. Under appropriate conditions, these plants go through their life cycle in about 36 days [36]. The result is that the techniques of selection, mutation and breeding can be carried out over a much shorter time-scale than with normal plants. Although these rapid-cycling strains of *Brassica rapa* are not themselves suitable for growing in the field, they belong to the same species as Chinese leaves and turnips. By cross-breeding, any characteristics selected in `fast plants` can be introduced into the crop plants. The choice of Chinese leaves or turnips depends on whether metal accumulation occurs in the shoots or the roots of the plants.

2.1. Toxicity tests

To test the range of metal ion concentrations which affect the germination of *B. rapa*, filter paper was partially submerged in 100cm^3 beakers containing the following metal ion solutions: 10, 50, 100, 500 and 1000 ppm of Cu^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}. All solutions were made from metal nitrates dissolved in deionised water and the pH adjusted to approximately 7 by addition of NaOH. 10 seeds were placed on the filter paper above the surface of the solution and the beakers covered. The beakers were placed under continuous lighting (see next section) at a temperature of 25±3 °C for 7 days.

2.2. Selection of Cu^{2+} tolerant/accumulator strains of *B. rapa*

For a preliminary study aimed at selecting strains of *B. rapa* which would grow on soil containing high levels of a metal ion, it was decided to utilise Cu^{2+} ions, which are not very hazardous for handling in the laboratory. The maximum concentration of solution chosen for study was 100ppm which is significantly toxic to plants. Seeds of *B. rapa* were grown under standard conditions to obtain a complete life cycle in about 35-40 days [36, 37]. They were placed individually in polystyrene pots containing approximately 7 cm^3 of soil which was a 1:1 (v/v) mixture of sieved peat moss and fine horticultural vermiculite. Three slow release NPK fertiliser pellets were added to each pot. Moisture for the seeds was provided initially by adding approximately 2cm^3 of deionised water to the top of the pots on each of the first 3 days. The bases of the pots were kept moist by capillary matting placed in contact with either deionised water or a solution of $Cu(NO_3)_2$. Approximately 50 seeds were tested on each of the following concentrations of Cu^{2+} ions: 100, 10, 1, and 0.1 ppm as well as on deionised water. All seeds were maintained at a temperature of 25±3 °C and under continuous lighting provided by a bank of fluorescent lamps [36].

Those plants growing strongly were pollinated after 15-18 days, whenever possible by means of self-fertilisation. Since the strain of *B. rapa* used in this experiment was normally self-incompatible, self-fertility was induced by the addition of several drops of a 1.5% (w/w) solution of NaCl to the stigma of a plant 15 minutes before pollen from the anthers of the same plant was transferred to the stigma [38]. In case of failure of self-pollination, some plants were cross-pollinated with plants of similar strength of growth on the same medium. Pollination was repeated three times over three days. After pollination was completed, non-pollinated flowers were removed from the plants to ensure that energy was channelled into seed production. Plants were grown for approximately 20 more days, removed from their growth medium and dried on top of the light bank. The seeds were harvested and were immediately planted to form the next generation. This second generation of plants was grown on medium containing 10ppm Cu^{2+} ions, with the exception of controls grown on deionised water. A similar process of selection, pollination and seed production was carried out and a third generation grown on medium containing 10ppm Cu^{2+} ions.

2.3. Mutagenesis

In an attempt to increase the chances of obtaining plants able to grow more strongly on soil containing Cu^{2+} ions, a sample of seeds and pollen from the first generation was treated with a mutagen [37]. Two methods, adapted from those used for other plants and for fungi, were employed [39, 40].

2.3.1. UV irradiation: Pollen and seeds were placed at a distance of 10cm under a cylindrical 6W UV lamp (emitting at 253.7nm) for a period of one to three hours. The pollen was used to fertilise the plant from which it was taken. The seeds were planted as described above.
2.3.2. Chemical mutagenesis: Seeds only were presoaked in deionised water for two hours at room temperature (25 °C). The water was then decanted and the seeds covered with a 1.5% (v/v) aqueous solution of ethyl methanesulfonate (EMS), an alkylating agent known to cause mutation. The seeds were left in the solution at room temperature for 5 hours, after which the solution was decanted and the seeds washed several times with deionised water. When the seeds had dried for 8 hours on the light bank, they were planted as described in section 2.2.

2.4. Cu^{2+} ion analysis

After the seeds had been harvested in each generation, all plants were analysed for their Cu^{2+} ion content [36]. Every plant was separated carefully from the soil, the roots washed using deionised water from a wash-bottle and then dipped into deionised water in a beaker. The plants were left to dry in air for three days on top of the light bank and then oven-dried for 24 hours at 105 °C.

2.4.1. Scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDXA)

Sample plants were examined using a Cambridge Stereoscan S90 SEM with EDXA. Roots, stems and leaves were separated, attached to double-sided adhesive film, placed on aluminium sample holders and coated with an anti-static carbon-based spray. Using the EDXA facility, a semi-quantitative analysis of elements present was obtained for each plant sample.

2.4.2. Atomic absorption spectroscopy (AAS)

To obtain a quantitative estimation of the amount of Cu^{2+} ions in each plant, AAS was carried out. Plants were dried as described above and ashed in a covered crucible at approximately 600 °C. The ash was digested in 20% HNO_3 and the resulting solution filtered. The residue was washed three times and the filtrate made up to 25 cm^3 in a volumetric flask. Samples were then tested using a Perkin Elmer AAS (Analysis 100 Model).

Since the amount of ash obtained from individual plants was generally too small for AAS analysis (<0.005g), ash from similar plants was combined to produce a larger sample (approximately 0.04g).

3. RESULTS

3.1. Toxicity tests

The results are presented in tables 2(a) & (b). In all cases tested, 1000ppm solutions of metal ions inhibited germination. On 500ppm solutions, stunted growth occurred for Cu^{2+} and Mn^{2+} ions, a very small amount of root growth (no shoots) for Pb^{2+} ions and no germination at all for Ni^{2+} and Zn^{2+} ions. At levels of 100 down to 10ppm, metal ions generally had some inhibitory effect on germination. The effect of Cu^{2+} ions could also be seen by the colour of the leaves which tended to be purple

It should be noted that these tests only indicate conditions for germination. Continued growth requires the presence of NPK fertilisers.

Table 2(a)
Growth of roots during 7 days (showing maximum growth achieved and time taken)

Concentration of metal ion (ppm)	Cu^{2+}	Mn^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
1000	stunted 2mm in 2d	very stunted dies back	0	0	0
500	few mm in 5-6d	1cm in 2-3d	0	very stunted in 2-3d	0
100	few mm in 3d	1cm in 2-3d	stunted few mm in 6d	1cm in 5-6d	0
50	2cm in 2d	1cm in 2-3d	1cm in 2d	>2cm (branched) in 4-5d	1cm in 2d
10	2cm in 2d	several cm (branched) growing still	1cm in 2d	1cm in 3d	1.5cm (branched) in 5-6d
0 (water)	5-8cm (highly branched) growing still				

Table 2(b)
Growth of shoots during 7 days

Concentration of metal ion (ppm)	Cu^{2+}	Mn^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
1000	0	0	0	0	0
500	1/3 seeds stunted; rest no shoots	closed green leaves	0	0	0
100	closed green leaves	N	0	N	0
50	half-open green/purple leaves	N	N	N	shrivelled pale leaves
10	open purple leaves	N	N	N	N
0 (water)			N		

N = normal, strong growth (green leaves formed within 3d, open within 4d)

Table 3
Height (mm) of first generation plants growing on soil containing Cu^{2+} ions

No. of days of growth	100	10	ppm Cu^{2+} 1	0.1	0
15 (Average height)	40	45	50	55	80
15 (Maximum height)	85	85	110	160	105
28 (Maximum height)	160	130	140	130	110

3.2. Selection of Cu^{2+} tolerant/accumulator strains of *B. rapa*

For the first generation of plants, strong growth was observed after 11 days for plants in soil on deionised water, 0.1, 1 and 10ppm Cu^{2+} ion solutions. Plants growing on soil watered by 100ppm Cu^{2+} ion solution were stunted and purple in colour. By 15 days, plants were ready for pollination. At this stage, plants grown on deionised water were on average taller than those grown on any of the Cu^{2+} ion solutions (see table 3). However, there were some tall, strongly growing plants on these solutions.

After 28 days' growth on 10ppm Cu^{2+} in the second generation, some very tall plants were obtained up to 220mm in height (compared with the maximum of 130mm achieved in the first generation) and, in the third generation, up to 340mm.

3.3. Mutagenesis

In general, the mutation conditions using EMS, described in the experimental section, were too severe and resulted in death of the seeds. In the case of UV irradiation, some of the treated pollen led to production of seeds which germinated in the second generation. Irradiated seeds also gave rise to plants in this generation. However, none of the plants produced in this way showed an increase in ability to grow on soil containing Cu^{2+} ions.

Much larger populations of pollen/seeds need to be tested to see if this technique is viable.

3.4 Cu^{2+} ion analysis

Using SEM/EDXA, it was shown that Cu^{2+} ions were present in higher concentrations in the roots of *B. rapa* than in the stems or leaves (see table 4). Therefore, for the removal of Cu^{2+} ions from the soil, it would appear necessary to produce a root crop, such as turnip, rather than a leaf crop.

Table 4
% Cu in different parts of *B. rapa* measured by EDXA

Concentration of Cu^{2+} in growth medium	Root	Stem	Leaf
10ppm	0.96	0.42	0.51
100ppm	6.55	0.63	0.08

When similar plants were grouped together to provide sufficient ash for analysis by AAS, increasing amounts of Cu^{2+} ions in the growth medium appeared to result in increased uptake of Cu^{2+} ions by the plant. However, there was insufficient ash for the analysis of individual plants which had shown increased growth on Cu^{2+} containing soil, although there was some indication of increased Cu^{2+} ion uptake in one group of plants.

4. CONCLUSIONS

The work described here was a feasibility study for a larger programme of plant breeding. The ability to select plants able to grow strongly on soil containing Cu^{2+} ions has been demonstrated together with a number of techniques to produce and analyse plants with higher than normal Cu^{2+} ion uptake.

Further work is planned to select plants on a considerably larger scale and for more generations. The advantage of using `fast plants' is their rapid life cycle which allows about 10 generations to be bred in one year. Using classical methods of mutagenesis and breeding avoids the present controversy arising from the production of transgenic plants (GMOs). However, in future, some of the modern techniques of genetic manipulation could be used in *B. rapa* and would have considerable potential.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Studies on Crystalline Rice Husk Ashes and the Activation of their Pozzolanic Properties

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Characterization, pozzolanic activity determination and pozzolanic activation of rice husk ashes (RHA) containing a high percentage of crystalline silica have been carried out. Two RHA samples from incineration plant and another RHA sample from energy-recovery combustion plant have been compared. Several techniques such as X-ray diffractometry, solubility in boiling KOH solution, conductivity and thermogravimetric monitoring of RHA/lime systems and strength development of RHA/cement mortars have been used for evaluating pozzolanic activity or RHA. Additionally, mechanical treatment of RHA by grinding and increase of curing temperature of RHA containing mixtures became appropriate procedures for activating pozzolanic activity of highly crystalline RHA. The effectiveness of chemical activators such as NaOH solution and powdered $Ca(OH)_2$ also was studied.

1. INTRODUCTION

Rice husk is an agro-waste material which is produced world-wide in about 100 million of tonnes. Most of the production [1] is in Asian countries (India, China, Thailand, Bangladesh). In Europe, Spain in the most important producer country of rice, and 100000 tonnes of rice husk are available for disposal.

Approximately, 20 Kg of rice husk are produced for 100 Kg of rice. Rice husks contain [2] organic substances (cellulose, lignin, fibre) and 20% of inorganic material (see figure 1), mainly silicon dioxide (SiO_2>85%). Two ways are stated for removing organic matter from rice husks: a) combustion with energy-recovery; and b) incineration. Because of the high silicon dioxide content, rice husk ash (RHA) may be used as cement replacement material. The silicon dioxide is able to react towards hydrated lime, $Ca(OH)_2$, for yielding hydraulic products (pozzolanicity). The pozzolanic activity of RHA depends on several parameters. The most important property of RHA that determines pozzolanic activity is the amorphous phase content [3]. When combustion temperature in higher than 600°C, partially crystallised RHA is obtained and, consequently, its pozzolanic activity becomes very low.

We present in this paper, the study of the reactivity of crystalline RHA and the activation of pozzolanic properties in Portland cement and hydraulic lime systems.

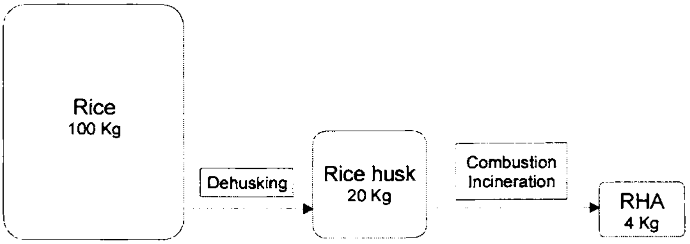

Figure 1.- Weight relationships in RHA production.

2. EXPERIMENTAL SECTION

Portland cement was a CEM I 52.5 R type cement. RHA samples were supplied by Agrocítrica (Alzira-Spain). Fine aggregate was siliceous natural sand, with 3.51 fineness modulus. Superplasticizers used were Sikament-300 (lignosulfonate based additive) and Glenium 22 from Bettor (melamine sulphonate based additive). Thermogravimetric analysis were performed in a Mettler-Toledo TGA 850 module, equipped with an ultramicro balance (resolution of the balance: 0.1µg), with a horizontal furnace. 70 µL alumina crucibles were used and dry nitrogen was the surrounding atmosphere (75 mL/min gas flow). The heating rate was 20°C/min in the 35-600°C range.

A Crison microCM2201 conductimeter was used for conductivity measurements of RHA/lime suspensions [4-6]. The measurements were carried out at 40°C, dissolving 80 mg of hydrated lime (analytical grade) in 100 mL of water, and adding 2000 mg of RHA. A X-ray PW1710 diffractometer was used for mineralogical characterization of RHA (CuK_α radiation, 40kV and 20mA). RHA samples were ground using a laboratory ball-mill (Gabbrielli ball-mill) with 18 mm diameter alumina balls.

3. RESULTS AND DISCUSSION

3.1 Characteristics of rice husk ashes (RHA)

The resulting ashes after organic matter removal contained a high percentage of silicon dioxide. Three samples of RHA were selected for experimental studies: two samples from an incineration plant without energy recovery, which presented a different crystallization (RHA-1 and RHA-2 samples). A third sample was collected from a combustion furnace used for dehydrating food for animals (RHA-3 sample) Chemical compositions for RHA samples are summarized in Table 1.

The samples obtained in the incineration plant (RHA-1 and RHA-2) showed lower loss on ignition values, due to more effective organic matter removal. In fact, RHA-3 was a black ash whereas the colour for RHA-1 and RHA-2 was grey.

Table 1
Chemical composition of RHA samples (%)

	M	LOI	IR	SiO_2	K_2O	Na_2O	P_2O_5	SO_3
RHA-1	0.04	0.46	7.21	89.39	0.24	0.52	1.06	0.53
RHA-2	0.29	3.00	6.44	85.69	0.48	0.68	1.24	1.20
RHA-3	0.64	6.99	6.60	83.51	0.25	0.22	1.21	0.35

M: moisture; LOI: loss on ignition; IR: insoluble residue after treatment with hydrofluoric acid

The presence of crystalline forms of silica in the RHA was determined using the X-ray diffraction technique. X-ray patterns for studied RHA are depicted in Figure 2. All samples showed peaks due to the presence of crystalline silica forms. Cristobalite and tridimite were found for RHA-1 and RHA-2, suggesting that the incineration temperature was greater than 900°C and/or temperature in 700-900°C range was maintained for a long period. On the other hand, RHA-3 sample only showed cristobalite peaks, probably due to lower combustion temperature. A typical diffuse band for amorphous silica in the $2\theta=21\text{-}25°$ range did not appear in the samples, suggesting the low percentage of amorphous silica material (disordered Si-O structure as a consequence of decomposition and sintering of hydrous silica without melting and crystallization) [3].

The morphology of RHA particles was studied by scanning electron microscopy (SEM). Micrographs of RHA samples are showed in Figure 3. In general, the internal structure consists of a skeletal structure of the husks, showing a large amount of microporous.

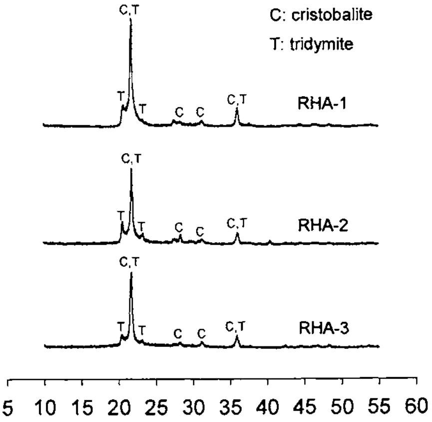

Figure 2. X-Ray diffraction patterns for RHA samples

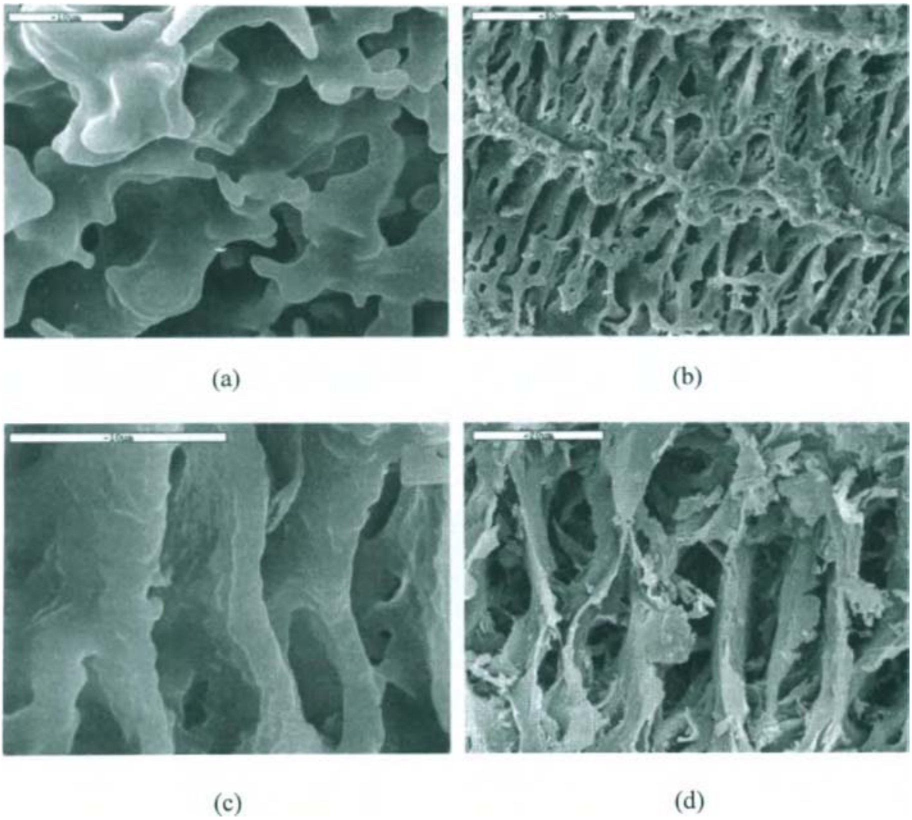
(a) (b) (c) (d)

Figure 3. SEM micrographs for RHA: a) RHA-1; b) RHA-2; c) RHA-3; d) amorphous RHA

This highly cellular was found also in amorphous RHA obtained in a laboratory furnace at 600°C (See Figure 3d). However, the walls of the cells observed in Figure 3d were more acute, in contrast to rounded edges in crystalline RHA. Probably, the temperature reached for crystallized samples produced a macroscopic arrangement of SiO_4 units at the RHA surface.

The amorphous silica content was evaluated by treatment with boiling KOH solution [1]. The dissolution of amorphous SiO_2, in these conditions, took place in the first minutes of the thermal treatment; crystallized matter will be dissolved for longer treatment times. Thus, Figure 4 represents the amount of SiO_2 dissolved for fine powder quartz at different times in these conditions: in the first 6 minutes, amorphous silica is rapidly dissolved (SiO_4 moieties in the boundary of the quartz grains). After this period, crystalline silica was slowly dissolved. The amorphous silica content measured in this conditions was similar for RHA-2 and RHA-3 (26.73 and 26.64% respectively), whereas RHA-1 became more crystalline (only 13.99% of glassy matter).

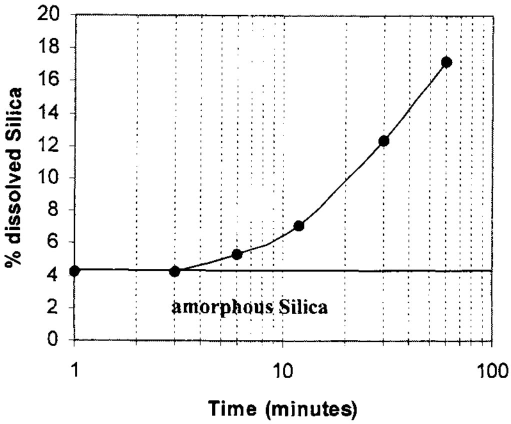

Figure 4. Dissolution of fine powdered quartz in boiling KOH solution: dependence with treatment time.

3.1. Reactivity of RHA towards hydrated lime and pozzolanic activation

In order to study the reactivity of RHA towards hydrated lime, several experiments were carried out: conductivity studies in RHA/lime suspensions, thermogravimetric analysis of RHA/cement and RHA/Ca(OH)$_2$ pastes, and, finally, strength development of RHA/cement mortars. Additionally, pozzolanic activity of crystallized RHA was activated by several procedures: mechanical grinding, curing temperature of RHA/cement pastes and mortars, and addition of chemical activators.

3.1.1. Mechanical activation

After organic matter removal, RHA consisted of large and low density particles, due to maintaniance of the original cellular structure. In these conditions, the ashes are not useful as cement replacement material because of the high water adsorption. The mechanical treatment of RHA using a ball-mill, produced particulate material of an adequate fineness. The results of the effect on particle mean diameter (d_m) for RHA-1 with grinding time are showed in Figure 5. Grinding-time in 5-20 minutes range reduced drastically d_m parameter. However, increasing of grinding-time did not produce important decrease in d_m for these grinding conditions. Subsequently, the effect of particle fineness of RHA from pozzolanic activity point of view in the RHA/cement system was studied by preparing mortars and measuring the compressive strength (R_c). The mortars were prepared as follows: 3/1/0.4 fine aggregate/binder/water ratio, being binder the amount of cement plus RHA; 15% of RHA replacement; use of superplasticizer (Sikament-300, 1% of the binder weight); 28-days curing time at 20°C immersed in water. Figure 5 shows the R_c dependence with grinding time of RHA. It is noted that 5-minutes grinding time is enough for an important activation of the

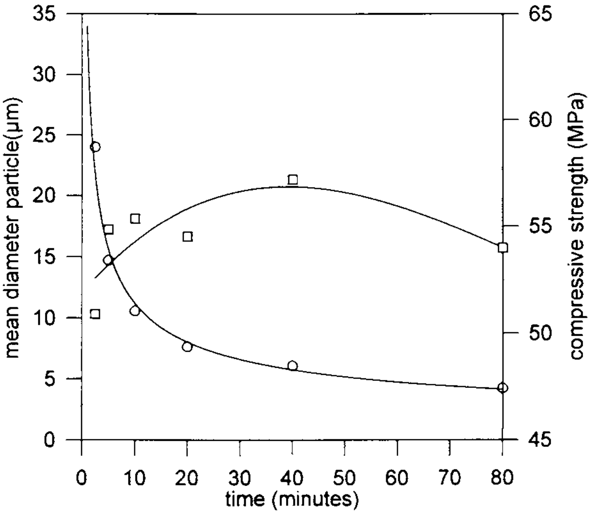

Figure 5. Effect of grinding time on RHA: (o)mean diameter particle and (□)28-day compressive strenght al 20°C

pozzolanic activity of RHA. The optimal grinding-time is near to 30 minutes, as shown in Figure 5. Longer grinding-times did not enhance mechanical properties of mortars, despite the increase in specific surface area of RHA.

3.1.2. Pozzolanic activity determination for RHA by conductivity measurement technique

Conductivity of RHA/lime suspensions were monitored according to the following experimental conditions: i) dissolution of 80 mg of $Ca(OH)_2$ in 100 mL of distilled water at 80°C; ii) cooling this solution to 40°C; iii) addition of 2000 mg or RHA; iv) conductivity monitoring of this suspension with magnetic stirring for 10000 seconds. Figure 6 plots the loss in conductivity curves for RHA studied. RHA-2 sample showed the higher effectiveness for lime fixation, finding approximately a 90% loss in conductivity at 10000 seconds. Despite similar vitreous silica content, RHA-3 only reduced the conductivity in 25% for the same reaction time. This result revealed the importance of the presence of unburned carbon on the surface of RHA particles: the carbon layer avoided alkaline attack to the siliceous matrix and, consequently, lime fixation at early age was diminished. As expected, RHA-1 sample was less reactive than RHA-2, due to its low amorphous content.

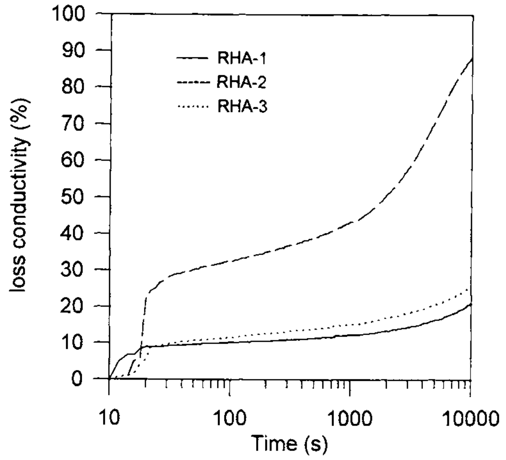

Figure 6. Loss in conductivity curves for RHA/lime suspensions at 40°C.

3.1.3. Curing temperature: thermal activation of pozzolanic reaction

The pozzolanic behaviour of ground RHA (5-minutes of grinding) was tested by thermogravimetric analysis of RHA/lime and RHA/cement pastes. The RHA/lime and RHA/cement ratios were 3:7, and pastes were cured at 20 and 40°C. Samples of pastes were taken out at 3, 7 14 and 28-days curing times. Figures 7 and 8 show the percentage of remaining $Ca(OH)_2$ for RHA/lime and RHA/cement systems respectively.

In figure 7, it can be noticed that the increase in curing temperature activated the RHA pozzolanic behaviour: the remaining $Ca(OH)_2$ decreased with the temperature increase for all RHA samples. At early ages, RHA-2 was the highest reactive ash, whereas at longer curing time RHA-2 and RHA-3 were similar at 40°C curing temperature. This indicates that similar vitreous content in RHA yields similar lime fixation at longer periods; however, the reactivity of RHA at early ages also depends on other parameters. Probably, the presence of higher amount of carbon in RHA-3 could make the pozzolanic reaction at early ages difficult, as proposed from conductivity experiments. On the other hand, in all cases, RHA-1 showed the lowest reactivity at any curing age, although also its pozzolanic activity increased with curing temperature.

In Figure 8, the percentage of $Ca(OH)_2$ for control paste (only Portland cement and water) was multiplied by 0.7 for comparing the curves with the same content of cement. At 20°C curing temperature, only RHA-2 showed a net lime fixation, whereas RHA-1 and RHA-3 yielded higher percentages than control sample, suggesting their role in the activation of cement hydration: RHA particles act as nucleating centres for hydration products from cement. This behaviour also has been observed for fly ash from thermoelectric power plants [7]. At 40°C, lime fixation was observed for all the RHA samples, being more important for the pozzolanic activity for RHA-2. The increase of curing temperature produced an increase of pozzolanic activity of RHA.

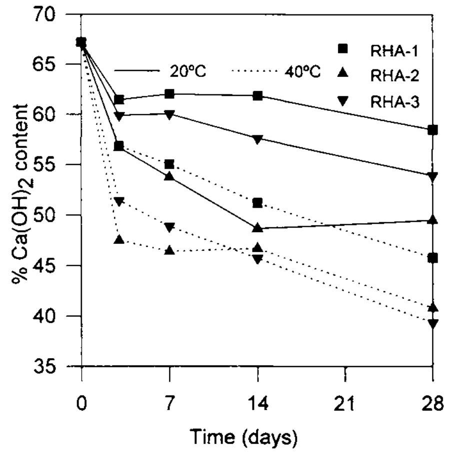

Figure 7. $Ca(OH)_2$ content for RHA/lime pastes

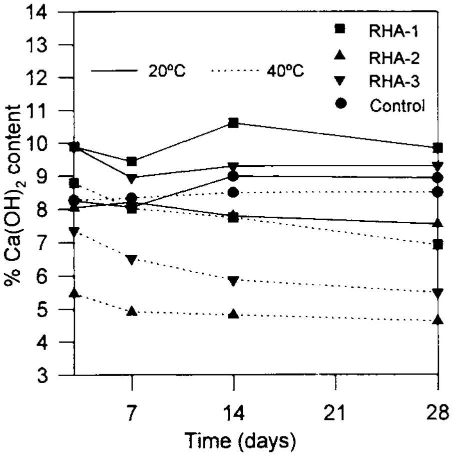

Figure 8. $Ca(OH)_2$ content for RHA/cement pastes (control curve has been multiplied by 0.7).

In a parallel way, compressive strength (R_c) of mortars (3:1:0.4 fine aggregate/cement/water ratio (Glenium 22 superplasticizer from Bettor, 1% of binder) were prepared using the highest crystallinity sample, RHA-1 (ashes ground for 20 minutes). Plain cement mortars (control) and 15% RHA-1 cement replaced mortars were cured at 20 and 40°C, and compressive strength (R_c) tested at 3, 7 14 and 28-days curing times. Figure 9 shows the R_i/R_o ratio values at 20 and 40°C respectively (being R_i the compressive strength for RHA-mortar and R_o the compressive strength for control mortar at the same curing age). It can be noticed that the influence of the presence of RHA in the hydration of cement: R_i/R_o values for early ages were greater than 0.85, indicating that RHA did not act as an inert material. For longer curing periods, R_i/R_o values increased, showing higher values for experience carried out at 40°C. Again, the temperature influenced notably in the development of pozzolanic reaction, despite the high crystalline silica content of the RHA tested.

3.1.4. The use of chemical activator

In order to increase the pozzolanic reaction rate of crystalline RHA-1, small amounts of chemical activators have been added when RHA-cement mortars were prepared. The chemical activators tested were: a) a 0.25 sodium hydroxide solution instead of water. Higher concentrations of sodium hydroxide were tested, finding a flash-set of mortars: this fact did not allow the specimens to perform adequately. b) Powdered calcium hydroxide, replacing 5% of cement. Mortars were tested in compressive strength development after curing at 20°C.

The compressive strength development for mortars with and without the additions are represented in Figures 10 and 11. In Figure 10, it can be noticed the presence of NaOH increased 1-day R_c values slightly. However, in the 2-day to 7-day period, R_c values were lower than those for mortars without this addition, indicating the negative role of the addition

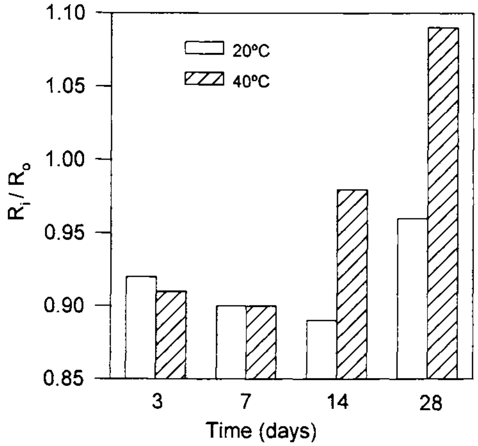

Figure 9. Relative compressive strength for RHA-cement mortars cured at 20 and 40°C.

and the none activation of RHA. The use of calcium hydroxide as chemical activator (see Figure 11) produced similar results.

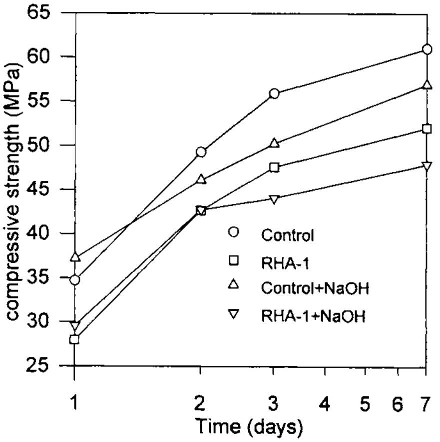

Figure 10. Compressive strength development for mortars with sodium hydroxide solution

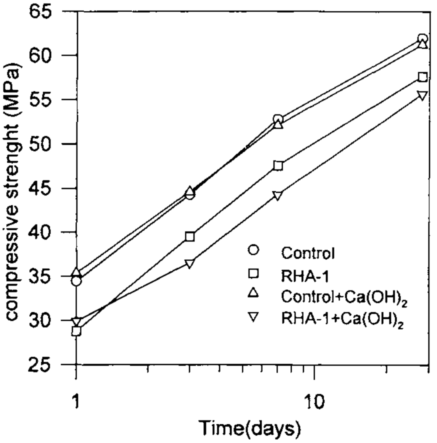

Figure 11. Compressive strength development for mortars containing calcium hydroxide

4. CONCLUSIONS

1. The application of several techniques for RHA characterization such as X-ray diffractometry, SEM, solubility degree in boiling KOH solution, permits one to establish the % of crystallization in RHA samples.
2. RHA grinding is a suitable treatment for enhancing pozzolanic properties of crystalline RHA. RHA samples with particle mean diameter in the 7-15 µm range showed good behaviour.
3. Conductivity monitoring of RHA/lime suspensions, and calcium hydroxide evolution measured by thermogravimetric analysis in RHA/lime and RHA/cement pastes, revealed the differences in reactivity due to crystalline content and the organic removal method used for preparing the RHA.
4. The increase of curing temperature from 20 to 40°C produced a beneficial effect on the pozzolanic reaction rate. At 40°C. lime fixation became very high at 3-days curing time, especially for RHA containing 25% of amorphous matter.
5. The presence of fine RHA particles increased the hydration rate of cement.
6. The thermogravimetric analysis monitoring is a good tool for studying the pozzolanic behaviour of crystalline RHA.
7. NaOH and Ca(OH)2 did not act as effective pozzolanic activators for crystallized RHA.
8. Despite the high crystallinity degree of the studied RHA, it can be used as a good pozzolanic material when fineness is high and mixtures are cured at a moderated temperature (40°C).

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Assessment of the Ecocompatibility of waste disposal or waste use scenarios : towards the elaboration and implementation of a comprehensive methodology

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The French concept of *"Ecocompatibility"* is defined as the situation where the pollutant flux from waste either disposed of or used in specified conditions (physical, hydrogeological, physico-chemical and biological conditions) is compatible with the environmental acceptance of the concerned receptor cells. The chief feature of this definition is to integrate the evaluation of the three following terms : *pollutants emission* from the waste (source term), *transport* of the pollutants from the waste to the receptor cells (transport term) and the *environmental acceptance* of receptor cells (impact term).

The specific objectives of our paper are the introduction of a methodology for the assessment of the Ecocompatibility of waste disposal or waste reuse scenarios and to develop the experimental part of this methodology : laboratory measurements and tests.

First, we introduce the various terms of the methodology. We briefly present a literature survey carried out by 9 research teams consisting of a state of the art on the knowledge and the tools available for the study of each determined term. This work particularly resulted in the identification of influence factors and characteristic parameters to be considered for a relevant assessment of waste ecocompatibility. An experimental programme (field and laboratory scale) followed the literature survey. It aimed to apply the methodology on 3 theoretical scenarios in view of the final methodology elaboration. Finally, we introduce the various steps of the defined methodology and conclude with its application limits.

Keywords : ecocompatibility, waste, disposal, reuse, impact, methodology.

1. INTRODUCTION

Waste disposal and waste reuse (e.g. : reuse of waste material for civil engineering or construction) are submitted to regulations which are mainly based on the best available technologies. They usually do not directly take into account the impact on human health and environment due to the lack of technical data in this domain. Recent emphasis on the need for evaluating this impact has resulted in the requirements for new evaluation tools.

In this framework, a research programme was launched by the ADEME (Agency for Environment and Energy Management) to develop a reliable methodology for evaluating the impacts of waste disposal or waste reuse scenarios. This programme is called "Waste Ecocompatibility".

First, the specific objectives of this programme were (i) to list the determining scenario factors and waste characteristics to be considered for a reliable ecocompatility assessment, (ii) to provide an overview of the available tools for measuring those factors and characteristics and, (iii) to propose a first approach of the methodology. This approach was then applied to 3 theoretical scenarios. This was part of the experimental phase of the programme (2 years). At the conclusion of this second phase, we defined a flexible methodology.

This experimental programme was presented at the international conference "Waste Stabilisation and Environment 99" in April 1999 [1][2]. In previous papers we detailed the field and laboratory experiments in view of a results comparative study [2][3][4][5]. Therefore, the work presented here only focuses on the elaboration and the implementation of the methodology.

2. SELECTED APPROACH FOR THE ASSESSMENT METHODOLOGY ELABORATION

2.1. Definition and general scheme of the Ecocompatibility concept

Considering the type of waste for which an ecocompatible situation can be expected very soon (final waste with mainly inorganic constituents) water was considered as the main vector for leaching and transporting the pollutant flux from the "source term" to the receptor cells. We assumed that the waste is placed in soil and in contact with water that flows past it and leaches contaminants from it.

The concept and definition of "Ecocompatibility" below can be stated as below :

Ecocompatibility is defined as the situation where the pollutant flux from waste either disposed of or used in specified conditions is compatible with the environmental acceptance of the concerned receptor cells.

The waste scenario will be considered as ecocompatible if (see figure 1) :

$F_{(A+B)'} < F_{C1}$ and $F_{(A+B)'} < F_{C2}$, where :

- F_{A+B} : is the pollutant flux of the couple (A + B) "source term",
- $F_{(A+B)'}$: is the pollutant flux reaching the surrounding environment after transfer and transport,
- F_{C1} : is the allowable pollutant flux in the aquatic medium,
- F_{C2} : is the allowable pollutant flux in the "soil".

Note : In this framework water is considered as the main vector of pollution.

According to this definition, the emission of pollutants to receptor cells depends on (i) the intrinsic pollutant potential of the waste (term A), (ii) the means of waste disposal in the environment (term B), (iii) the transport of the pollutant flux (term T) from the "source term" (A+B) to the receptor cells. The level of pollutant flux acceptable for the receptor cells (term C) mainly depends on the type of medium. Within the framework of this methodology the media judged the most relevant are the aquatic and soil media.

To achieve the programme objectives the study of these various terms was a joint work of 9 research teams. As mentioned above, the first step was a literature survey (1 year).

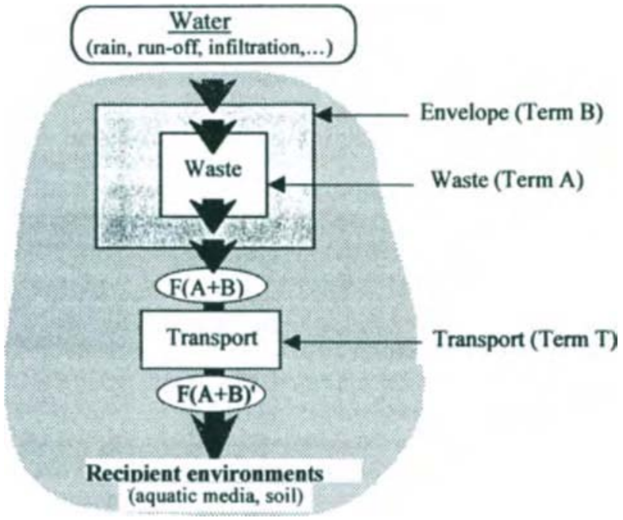

Figure 1. General scheme.

2.2. Literature survey

This survey aimed (i) to overview the scenario factors and the waste characteristics to be considered for evaluating ecocompatibility of a waste scenario, (ii) to state the available tools for measuring them, (iii) to identify the needs for further improvements, implementation and validation of the non standardised tools, and (iv) to focus on the new tools to be developed. The main objective of this part was to propose a first approach of the methodology.

Study of the intrinsic pollutant potential of the waste (Term A) : This part aimed to study the physical, chemical, mechanical and biochemical (microbial activities) influence on the pollutants release. The intrinsic pollutant potential of the waste was also studied through its ecotoxicological characterisation.

Study of the "envelope term" (Term B) : We called "envelope" the interface between the waste and the environment. This may be the way to depose it (dump...) but also a vegetable soil, a watertight system (covers...)... Indeed, the pollutant potential of a waste disposal or a waste reuse scenario also depends on the deposit conditions of the waste in the environment. The envelope controls the water in and output. Consequently, geotechnical aspects are crucial for determining the pollutant flux from the "source term" (we called "source term" the couple "waste/envelope").

Study of the "source term" (Term A+B) :

The influence factors and characteristic parameters to be considered for studying the "source term" are those previously identified for both terms A and B. In real use or disposal conditions, the pollutant flux from the term "A+B" also depends on the "water/waste" contact which depends itself on the characteristics of term B.

Study of the "transport term" (Term T) :

This is a determining step for evaluating the pollutant flux that will really reach the receptor cells. This study particularly aimed to overview the existing models of pollutant dispersion in saturated or unsaturated media.

Study of the impacts on the receptor cells (Term C) :

The potential impact on aquatic medium was studied for surface water and groundwater. The potential impacts on the soil ecosystem was studied through specific biological targets : microbial population, earthworm population and plants.

Guidelines :

The literature survey led to a synthesis of the available tools and focussed on the most relevant ones. Obviously, all the influence factors and characteristic parameters identified are not relevant to each scenario. A selection of the most appropriate parameters is necessary for the ecocompatibility assessment. This selection is defined by the specific scenario conditions.

2.3. Experimental programme

In order to validate and improve this approach (described above), it was applied to 3 theoretical scenarios. One of these theoretical scenarios is presented in figure 2.

The programme was composed of :

- *laboratory experiments*, aiming to develop the tools necessary for the ecocompatibility assessment,
- *field experiments* to validate and calibrate these tools.

For field experiments, simulation of percolates was performed with field pilots (30 m^3) in which the studied scenario conditions were strictly reproduced : compacting, rainfall, drying-wetting cycles... Over 4 months, percolates were successively collected in view of the experiments on earthworms, soil micro-organisms, plants and invertebrates[1]. A detailed description of the experimental programme is presented in previous papers [1][2][3].

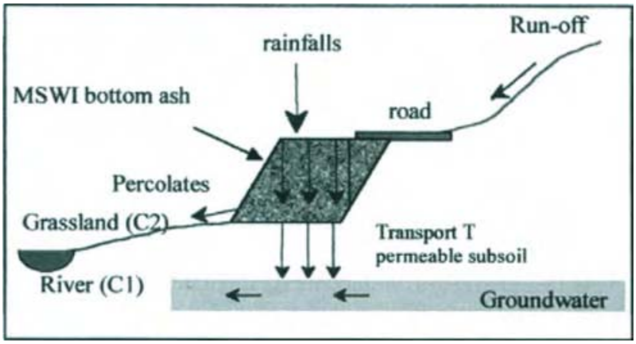

Figure 2. Scenario 1.

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[1] Field tests on aquatic media : experimental artificial streams [2].

3. INTRODUCTION TO THE PROPOSED METHODOLOGY

This methodology results from a joint project of the 9 research teams involved in the "Waste Ecocompatibility" programme.

The general steps in conducting the ecocompatibility assessment of waste disposal or reuse scenarios are described below.

3.1. Step 1 : preliminary description of the scenario

This step consists in a first description of the waste storage or reuse system, the target receptor cells and the significant study period. This description deals with the conditions which influence the release, the transport and the impact of pollutants. e.g. : waste description (origin, physico-chemical properties...), hydrogeological and weathering conditions, biological conditions, variation of these conditions versus time.

This is then followed by a description of the global scenario as a combination of subscenarios corresponding to each term (A, B, T and C). To illustrate this, we present the list of relevant subscenarios for term A in table 1. For example., the subscenario A1 represents the water percolation through a porous granular waste material.

Finally, we established a cross list "subscenario / the influence factors and characteristic parameters". This cross list specifies the appropriate the influence factors and characteristic parameters for each subscenario.

Table 1

relevant and realistic scenarios referring to term A

Nature of the waste	"Water/Waste" contact		
	Percolation	Wash off	Immersion
Porous granular	Subscenario A1	-	Subscenario A4
Porous monolithic	-	Subscenario A2	Subscenario A5
Vitrous granular or monolithic	-	Subscenario A3	Subscenario A6

3.2. Step 2 : identification of the influence factors and characteristics parameters to be considered

All the external factors and parameters are not relevant for each scenario. Those to be considered are selected by reference to the cross list "subscenario / influence factors and characteristic parameters".

This is a crucial step for determining the parametric tests to be implemented because they are defined by the selected factors and parameters.

3.3. Step 3 : implementation of laboratory tests and measurements

The tests to be implemented are parametric and simulation tests.

Parametric tests taking into account the influence of only one parameter. The parametric tests are used to measure an intrinsic property or to evaluate the effect of a given external parameter. The implementation of such tests enables us to supplement data from simulation tests and to explain the observed phenomena for a long term prediction.

Simulation tests taking into account the influence of the several parameters. These tests simulate the combined effect of various parameters. They enable us to reproduce at laboratory scale the field phenomena observed over a specific period.

Protocols :

At the conclusion of the literature survey we presented and described protocols of the parametric tests to be implemented for the ecocompatibility assessment. Some of these tests are already standardised (French or European standardisation). Others was validated during the experimental programme and can also be used.

Given the objectives of the simulation tests (to reproduce the field conditions at laboratory scale), a standardisation of the protocols is not to be expected as they are dependent on the studied scenario conditions. For the evaluation of "the source term" and "transport term" the current devices are : lysimeters, percolation devices (columns) or batch leaching reactors. Concerning term C, the simulation tests aim to reproduce the studied ecosystem (microcosms, mesocosms...).

Implementation of the tests and measurements :

The various steps in conducting tests and measurements are presented in table 2.

3.4. Step 4 : assessment of the global scenario ecocompatibility

This evaluation is based on the results of the tests and measurements. It also includes a discussion on the limits of this evaluation.

"Source term", results of the steps 1 and 2[2] *: characterisation and parametric tests :*

- Case 1 : The waste does not exhibit a potential hazard ⇨ the "source term" is considered negligible and the studied scenario is consequently judged "ecocompatible" ;
- Case 2 : The waste does exhibit a potential hazard ⇨ the evaluation procedure is continued, i.e. : step 3 of the "source term", steps 1 to 3 of the "transport term"...

Term C : "impact on aquatic media", "impact on soil faunae", "impact on soil micro-organisms", and "impact on soil plants" :

Bio-tests are selected according to the previously identified target environmental media (aquatic media and/or soil media). They are carried out on percolates[3] produced by the simulation test. According to the scenario conditions, percolates from the "source term" go through a soil transfer or not (see table 2 : steps 3 of the "source term" and "transport term").

Bio-tests are carried out step by step, and scheduled in a cost effective way. Each test ends with a results evaluation :

- Case 1 : The scenario is still potentially "ecocompatible" ⇨ the evaluation procedure is continued ;
- Case 2 : The scenario is not "ecocompatible" ⇨ the test sequence ends on a "non-ecocompatible" verdict.

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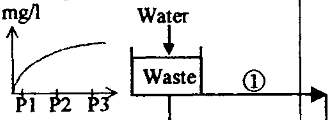
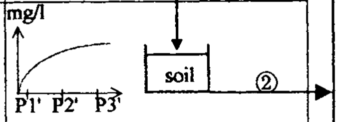
[2] The steps mentioned here are the same as those mentioned in the table 2

[3] It may be wash off or immersion instead of percolation.

Table 2

Steps in conducting parametric and simulations tests

Term A + B "Source term"	Step 1 : • Physical characterisation • Chemical characterisation • Intrinsic ecotoxicity	Step 2 : • Parametric tests selected for the leaching assessment : - physico-chemical study (ANC,...) - biological study - ecotoxicological study (tests associated to leaching tests)	Step 3 : • Simulation test (simulation of the main scenario characteristics) Ex : Lysimeter 
Term T "Transport"	Step 1 : • Physico-chemical characterisation of the soil (permeability, nature, chemical composition,...)	Step 2 : • Parametric tests selected for the transport assessment (hydrodynamic study, pollutants retention,...)	 Step 3 : • Simulation test Ex : Lysimeter
Term C_A	*Term C_A"Impact on aquatic media"* Step 1 : Tests on benthic and interstitial invertebrates (survival, post exposure survival). *Proposal for further investigations : study on other organisms (bacteria, alga, protozoae,..), effects on metabolism (respiration...), bio-accumulation and genotoxic study.* Step 2 : Tests on invertebrates in experimental artificial streams : faunistic composition (abundance and diversity) and emergence. *Proposal for further investigations : tests on other organisms in experimental artificial streams, tests with a longer study period.*		
Term C_{B1}	*Term C_{B1}"Impact on soil faunae"* Step 1 : Laboratory tests on Earthworms (*Eisenia andrei* and representative species) : study of biological parameters (survival, weight evolution, sexual maturity, fecundity, hatchability rate). *Proposal for further investigations : Study on other organisms (Collemboles,...).* Step 2 : Laboratory tests on Earthworms : study of behaviour parameter (feeding activity). *Proposal for further investigations : other tests on behaviour parameters, bio-accumulation study, genotoxic study.* Step 3 : Test on biodemographic parameters (mesocosms) : structure and diversity of the earthworm communities. *Proposal for further investigations : laboratory tests on reconstituted population with a longer study period (more than 1 life cycle).*		
Term C_{B2}	*Term C_{B2}"Impact on soil micro-organisms"* Step 1 : Quantitative approach (demography) : direct enumeration of bacteria, enumeration of the cultivable heterotrophic bacteria, enumeration of the specific cultivable bacteria (bacteria that fix atmospheric nitrogen...). Step 2 : Measurements of potential activities (nitrification, nitrogen fixing,...). Step 3 : Genetic structure of soil bacteria communities : diversity of functional genes. *Proposal for further investigations : impacts on the soil bacteria communities (RISA technique), tests with a longer study period.*		
Term C_{B3}	*Term C_{B3}"Impact on soil plants"* Step 1 : Study of the germination rate, study on biomass : aerial part and root system Step 2 : Study on the lack of nutrients (N, P, K, ...), bio-accumulation. *Proposal : impact on plant communities structure, phytogenotoxicity study.*		

①&② Use of P1, P2, P3 or P1', P2', P3' (waste+soil transfer) percolates depending on the global scenario conditions.

Thus, the evaluation procedure ends (i) if the "source term" exhibits a negligible potential hazard, the scenario is then "ecocompatible", and (ii) if the "term C" exhibits a potential impact, the scenario is then "non-ecocompatible".

4. CONCLUSION

The approach applied to elaborate the methodology, based on a literature study and on laboratory and field experiments, led to an operational methodology. It can be used for the study of new scenarios or the characterisation of existing scenarios (deposits, waste utilisation...). It can also be used as a decision-making tools for the conception of new storage centres or civil works compatible with the environment.

There are two main limits of this methodology. On one hand, some parametric tests are still not available for a few scenarios (e.g. scenarios concerning organic waste). On this other hand, it is not possible to carry out a systematic long-term prediction. Although we are still waiting for further investigations, this methodology is applicable for the medium-term behaviour assessment and the scenarios for which the experimental tools are already available and validated.

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Waste Materials in Construction
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Research & Development Methodology for Recycling Residues as Building Materials - A proposal

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This article presents a proposal of methodology for conducting such research and development. The data/statistics waste collection statistics phase must cover geographical distribution, seasonal variations on production rates, waste management practices, current applications and their related costs and revenues. Waste characterisation must be comprehensive with physical, environmental and chemical aspects, including waste variability and waste contamination from shipping, handling and storage activities. Based on the previous results a broad forecast of potential applications must be developed based on very simple rules like minimisation of transportation distances and energy consumption, etc. Marketing evaluation is a very important step, frequently neglected when choosing the best applications for a particular waste. Other steps are product development and performance evaluation. Environmental evaluation of the new technology is very important because not all recycling is environmentally sound. This evaluation must be based on the life cycle assessment (LCA) and has to consider the environmental benefit of avoiding landfill disposal of the waste and could include leaching or other specific tests or simulations. Also, the technological transference phase must be carefully planned and developed.

Each proposed step is discussed, examples are given and needs for further research emphasised.

1. INTRODUCTION

Without question it is very difficult to introduce new technologies into the building sector (PRIES and URIJTHOFF, 1989 and HESEGUER, 1989) and countries like the USA and Brazil which have very different socio-economic characteristics, have programs to help further the technology innovation in the building sector. There are various reasons, like prescriptive building regulations and the low impact of technology innovation on costs in the real estate business due to land prices. Additionally, at least in Brazil, users do not trust in new technologies due to unsuccessful past experiences.

At least two of these unsuccessful experiences are connected to recycled waste. During the 80's, an international company started marketing phosphogypsum based panels. Due to the content of phosphorus in the panels and the Brazilian climate (mild temperatures and high relative humidity) in less than one year contamination of the walls appeared. In no more than a year the technology was off the market.

The second example was an international environmental and public health disaster. In Germany, poultry meat that was contaminated with dioxin was found to be connected with a Brazilian poultry food named citric pulp. The citric pulp had been contaminated by a recycled lime sold as building material. This hydrated lime was a waste from a vinyl chlorine complex, owned by a Belgian company. After it was found that the waste was mainly calcium hydroxide and the lime fully complied with all Brazilian standards for hydrated lime, it was sold on the market for about 10 years. It was mainly used to produce plastering cement-lime mortars, for interior and exterior finishing. Hundreds of thousands of people are potentially exposed to health risks due to inadequate product development.

Successful research and development of a new building material or component using waste as raw material, is a very complex task. This task comprehends a multidisciplinary approach involving knowledge from different areas, such as materials science, marketing development, performance evaluation and environmental sciences. The Business Council for Sustainable Development–Gulf of Mexico (BCSD-GM), a branch of the World Business for Sustainable Development, emphasises that there are several barriers to recycling (BCSD-GM, 1997), other than the technical difficulties. They include economic, geographic and regulatory (or environmental), legal, business, social, time and informational barriers.

As the environmental benefit of the recycling will only be utilised by the society if the new product succeeds on the market (SKINNER, 1994), this methodology must include technical, environmental and marketing aspects. Nowadays the growing number of companies that adopt recycling as a vital tool for improving their business and environmental sustainability can easily be observed. The Business Council for Sustainable Development–Gulf of Mexico (BCSD-GM), developed the *By-product Synergy* concept. This concept emphasises that it is important to have a "synergy among diverse industries, agriculture and communities resulting in profitable conversion of by-products and wastes into resources promoting sustainability" (BCSD-GM, 1997). The EPA calls this same concept "Green Twinning". Recycling also plays an important role on *Eco-efficiency*, and other business oriented paradigm that have been adopted by several important multinational companies and business leaders. (DESIMONE & POPOFF, 1996).

It is possible to foresee that more and more researchers, engineers, marketing specialists, governmental staff members, etc. will be involved with the research and development of recycling technologies in the near future.

In this scenario, a comprehensive research and development methodology could be very useful in helping multidisciplinary research teams to work and communicate.

2. METHODOLOGY

A research methodology must be a logical guideline to help research teams carry out their tasks. The methodology must emphasise the important aspects to be considered and their interconnections. A methodology should be not be understood as a sequence of steps to carry out the actual R&D work.

2.1. Collecting available Waste data and statistics

The very first step of the research is to gather all available data about the waste.

2.1.1. Production statistics

An appraisal of the amount of waste produced at the industrial, regional, national or even world-wide levels is important for several reasons. The availability of the waste will outline both the market possibilities of the new product and the necessary structure to recycle it. The production of some residues is intermittent and frequently only happens during a certain period of the year. This is the case of most of agribusiness wastes. This effect introduces the necessity of having stockpiles in order to sustain the uninterrupted production of the recycled product or of having a special arrangement with business which makes it viable to operate on the same basis.

The geographical localisation of the different sources of the residue is also relevant. Transportation distance is a key aspect on the cost of production, mainly in large countries. Transporting waste for long distances is always subject to very strict control, which makes the process even more expensive or sometimes not even possible. Transportation also affects the environmental balance of the new product.

Having large amounts of the waste and several sources increases the relevance of the research and improves chances for the new product to succeed on the market (see technology transfer).

2.1.2. Regulatory aspects costs and destination

Studies of waste's legal status, its destination and all associated costs or revenues are relevant. It is common for a waste that is dumped on a landfill by one specific company to have a good market in another region. This happens because there is little or no exchange of information on waste management, except for the most commonly recycled wastes, or due to market characteristics or diverse legislation.

The total cost of managing a waste is normally a good way to calculate the interest for its recycling and is always a strong argument when asking for financial support. If the waste doesn't have a significant cost or isn't the object of social pressure, there is probably little interest in recycling from the producer's point of view.

Regulatory aspects can limit waste recycling and even waste transportation. Consequently, a detailed study of all legal status of the waste is very important.

2.1.3. Residue production process

A careful study of the waste's production process, including its variability, normally gives significant information about its characteristics, including its probable composition, and even about the possible presence of contaminants like dioxins or heavy metals.

There is more than one production process for most materials and, consequently, more for wastes. Frequently, these differences can result in wastes with very different characteristics despite having the same name. One very well known example is steel slag, a generic name that embraces a myriad of chemical and mineralogical compositions, that affect its recycling opportunities. Combustion ashes produced in a fluidised bed boiler, have completely different physical, chemical and mineralogical characteristics than those produced in a static oven.

Sometimes the same generic name is given to products of very different processes, simply because they have the same basic chemical composition. This is the case of the term "artificial gypsum", which depending on the author's intentions can include both phosphogypsum and chemical gypsum produced by desulphurization processes. SAKAI and MASAKATSU (1997) and LAMERS and BORN (1997) show the influence of the different municipal solid waste incineration technologies on the environmental quality of the molten product by use of leaching tests.

Even a small variation on production process parameters or raw materials sources or composition can result in significant changes on residue characteristics. Boiler temperature, for instance, controls the glass content of siliceous ashes.

A good bibliographic review is normally a good starting point for this step. However, it is essential to enhance this information with a study of the actual production process, preferentially with the support of a specialist in the field.

2.1.4. Waste composition and presentation

Most industries have little information about their own waste except those legally required to do so by the environmental agencies, e.g. environmental classification after leaching tests. Therefore, most of the time the available information will be useful only as a starting point for a deeper study.

Post-production management which varies greatly from company to company has an essential influence on waste composition and presentation, affecting its recyclability (WBCSD, 1998). Ashes, for example, can be removed from the oven by whirlwinds or water. In the case of blast furnace slag, the existence or not of a quenching process like granulation or pelletization affects its chances for recycling.

If a residue is not intended to be recycled, it is frequently dumped in the same bin with others, resulting in serious contamination. Due to a plant design limitation or even cultural aspects, it could be very difficult or even expensive to change the established managerial procedures.

2.2. Waste characterisation

Characterisation of the waste must be as complete as possible. The data collected in the previous step is very useful in guiding the selection of the most important aspects of characterisation.

This phase must include:

(a) the complete chemical composition including environmentally relevant trace species, humidity and volatile content;
(b) its microstructure, including the mineralogical composition, such as glass content and different phases, porosity and morphology;
(c) physical characteristics like density, granulometry, viscosity, and
(d) environmental characterisation, including its toxicity, ignitability, corrosivity, reactivity as well as its pathogenic potential by using appropriate methods such as leaching and volatile organic compound tests.

Microstructure characterisation, despite being frequently neglected, is very important because inorganic residues can have unstable mineralogical phases.

It is important to determine waste composition variability . Sometimes the composition is affected by a change in source of raw materials. Table 1 presents the variability of steel slag composition during one-day production. Some phosphogypsum can be radioactive, depending on the raw material source. Coal ash has been recycled as cement admixture since 1935 (DAVIS *et al.* *apud* MALHOTRA (1994) and is usually classified only on the basis of its major oxide composition, such as Si, Ca, Mg and Al_2O_3 content, like on ASTM classification. MEJI (1997) shows how small differences in trace element content, such as Br, Cd, Ge, Mo, Pb, of coal can affect the environmental quality of the different ashes produced. The author presents a coal classification of ashes based on its raw material trace elements composition, allowing a forecast of the environmental quality of the ashes.

Table 1
Variability of the basic composition of steel slag (USIBA-Brazil) during one day. (%)

	CaO	SiO_2	Al_2O_3	MgO	TiO_2	FeO	MnO	P_2O_5	S	Cr_2O_3
Max.	58,56	28,42	6,41	9,87	0,5	32,94	5,03	0,844	0,244	0,508
Min.	34,12	14,98	2,38	6,69	0,33	0,98	0,08	0,318	0,00001	0,045

Alterations of the industrial process, such as temperature changes, waste treatment procedures, etc. can affect the residue characteristics as well. LAMERS & BORN (1997) present a good example of this effect on environmental performance of municipal waste incineration residues.

This is a very important stage because only a good knowledge about the residue and its variability allow for selecting the recycling technology that will give the best technical and environmental results. This step must involve several different characterisation technologies and scientific knowledge areas.

2.3. Selection of possible application

The goal of this step is to select the best potential uses for recycling the waste. As a rule, the best application for the waste is the one that will use its true characteristics and properties to enhance the performance of the new product and minimise environmental and health risks. Waste applications should not be made on a preconceived basis. This requires creativity and a wide range of both scientific and technical knowledge and for the best results will require the collaborative work of a multidisciplinary team. The WBSC-GM (1997) stresses the importance of being innovative on recycling technologies. Even when a waste has more than one well established recycling technology there are always other options, that eventually can be more efficient in a specific situation. CATALFAMO, PASQUALE & CORGLIANO (1997), for example, suggest that it is possible to recycle coal fly ashes as zeolitized products and as heavy metal absorbers. JOHN & TINKER (1996) presents a Internet database that collects recycle opportunities to different wastes.

Recycling is always one of the options for waste management and only makes sense if it is the alternative that minimises the environmental impact as a whole, including the new recycled product life. TUKKER & GIELEN (1994) present a methodological scheme to evaluate the environmental benefits of different options, including the life cycle evaluation of the different options. At this stage of research, evaluation of the recycling alternative can be done in qualitative terms. ONG, KOH and NEE (1999) present a tool for a semi-quantitative pre-LCA.

One alternative approach that simplifies the work is to consider some rules:

(a) minimise the need for industrial transformation of the waste;

(b) minimise the transportation impact of the waste to the industrial plant and the produced material to its consumers;

(c) for those containing dangerous chemical compounds, recycling must minimise the leaching or volatilisation of these this dangerous phase, by avoiding contact of the new product with the users or any deterioration agent, such running water;
(d) the new product must be recyclable;
(e) the new product must present a competitive advantage in comparison to those competitors already established on the market and improve the waste value.

For each application, a different group of characteristics is advantageous or even essential. A predominantly organic material can be recycled as fuel on different burning processes, including as an alternative source of energy on cement kiln. A granular waste can be applied as aggregate to concrete production if it is dimensionally stable, does not present any harmful reaction with hydrated cement phase constituents, is water insoluble and has compatible mechanical strength. In order to be suitable for recycling as binder material, a waste must:

(a) be soluble in water or in strongly based pH water;
(b) have Ca, Si, Al, S elements as major components;
(c) be presented in a granular form, preferentially with a high surface area;
(d) for those on Si is an important constituent, like most ashes or melted products, a high glass content is desirable.

A database presenting the requirements for different applications can be very useful for researchers.

At least as a first approach, the ideal situation is the use of the residue as a material without any industrial transformation. An industrial activity requires energy, and most of the time, generate residues. Therefore, recycling this to a minimum improves the environmental balance of the recycling activity. It also potentially reduces the amount of investment needed to build the production plant, which can simplify be an important constraint to the technological transference.

Reducing the environmental impact of transportation is equally important. Transportation has environmental and financial impacts and there are legal restrictions on the transportation of waste especially, the most dangerous ones.

Recyclability is mandatory for any eco-efficient design (DESIMONE and POPOFF, 1998) and it is much more important if the waste incorporates dangerous compounds to avoid the risk of landfill disposing the material after its service life.

The competitive advantage is very important because, it weighs heavily on the success of the developed product on the market. Applied to products the competitive advantage position can mean a lower relative cost for a product with the same or a superior performance or customer value (DAY and WENSLEY, 1989). Ideally, is the detection of a market application without any established competitor is desired but most of the time this is hard to find. Marketing segmentation is also a good strategy. Identifying customer subgroups can be defined as a strategy (HALEY, 1989) or a special application where the new product is potentially more efficient than the traditional market solution. In this strategy, it is very important that the planned research and development activity succeed in order to demonstrate these advantages over the traditional solutions. The amount of waste available is frequently a limitation for some applications.

Developing an application which adds more value to the waste is also important (CORNELISSEN, 1994) because it increases the financial appeal for recycling. The recycling of granulated blast furnace slag or fly ash as concrete admixture is, nowadays, much more than an alternative for reducing costs (CORNELISSEN, 1997, BIJEN, 1996, MALHOTRA, 1994). Other reasons are an improvement in concrete performance, including durability, and reduction of the environmental impact of the concrete.

Most of the time there is more than one viable technology for recycling a waste. If at this stage more than one technology seems to be viable, a multiattribute decision method, like the Analytic Hierarchy Process (SAATY, 1994), can be used to help find the most suitable application.

2.4. Development of new product

Concurrent engineering can be a very important concept in this phase. It emphasises that product development must simultaneously take into account production technology, product performance, maintenance, reliability, market competitive issues and environmental impact, all in a cradle-to-grave approach (SWINK, 1998).

Development of the new product must be done on a scientific basis. In order to reduce uncertainty, the behaviour and characteristics of the new product must be explained in terms of its microstructure, chemical reactions, etc.

It is very important to understand the new product's durability. This can be achieved by investigating the degradation mechanisms and factors of the new product (SJÖSTRÖM, 1996). Durability is very important because it affects both environmental and economic performance. Additionally the chemical and physical changes that results from the degradation process can affect environmental behaviour like leaching performance.

Development must focus on the customer and the environment. For building products, the ISO/CIB performance methodology is very useful for evaluating end use customer satisfaction from a technical point of view. It is based on typical user requirements lists, that is generic and, of course, non-exhaustive (Table 2). The cradle-to-grave concept is not totally incorporated in this methodology and requirements like maintainability, upgradeability (JOHN, KRAYENBRINK, VAN VAMELEN, 1996) can be incorporated in the same concept.

The performance methodology is a very valuable tool for helping with evaluation of design decisions on fitness of purpose for the new product. Most countries have performance based specification and evaluation methods for most building components, which makes the evaluation easy.

Table 2
CIB/ISO users' needs (CIB, 1983)

Structural stability	Acoustical comfort
Fire safety	Tactile comfort
Safety in use	Anthropodynamic comfort
Watertightness	Hygrothermal comfort
Air purity	Visual comfort
Hygiene	Suitability for use
Durability	Economy

Performance methodology also helps to demonstrate the superior performance competitive advantage. Frequently a new product, e.g. a masonry block, is evaluated from a technical point of view using only a concrete block standard. The environmental risks of this approach are obvious. But the technical risks are also important because the standard was developed by taking into account the characteristics of the traditional solution and not the required performance of the application (CIB, 1983).

The effect of the waste and other raw materials variability on the performance of the product must be considered. The variability can be controlled by raw materials homogenisation techniques during the handling phase. Recyclability must be assured at this stage, especially if the waste contains hazardous components.

Marketing considerations can be taken in order to better adequate the product to its market segment, production costs, and life cycle costs. In considering the cost of recycling it is important to consider the difference between the cost of disposal in a landfill and the recycling cost (SKINNER, 1994).

The environmental impact of design decisions can be evaluated using the qualitative pre-LCA methodology.

2.5. Product evaluation

2.5.1. Performance evaluation

After the development of the new product and its process of production are finished, a complete performance evaluation is needed. This evaluation allows demonstrating its fitness for purpose and its advantages in comparison with the main market competitors. Evaluating the durability of the new product is probably the most complex task in this phase. Performance evaluation can also highlight the need for further improvements on the product.

Applying for a performance evaluation based technical approval issued by an independent body can increase market acceptance of the new product. (HEWLETT, 1996).

2.5.2. Environmental evaluation

The purpose of this step is to evaluate the global environmental impact. It is always important to put the evaluation into perspective by making a comparison with the traditional market solutions on the same basis.

Environmental contamination risk evaluation due to leaching of hazardous components is mandatory (KOSSON & VAN DER SLOOT, 1997; HOHBERG *et all.,*1997) but it is not sufficient. Other environmental impacts like greenhouse gases emission, human toxicity, acidification, energy use, etc. are also important and good technology for recycling frequently allows significant reduction on these impacts. Recycling blast furnace slag as a cement admixture allows for a very significant reduction of CO_2 emission during the cement production process, for example. The environmental evaluation must be carried out using life cycle analysis on a cradle-to-grave basis. AZAPAGIC (1999) and SCHUURMANS-STEHMANN (1994) summarise the methodology of life cycle analysis. TUKKER & GIELEN (1994) present an approach for the environmental evaluation of waste management benefits, including recycling.

The effect of degradation processes on leaching and other environmental impacts must be evaluated as well.

The probable destination of the new product after the end of its service life is very important. If the product can be delivered to a landfill, it will probably be ground. This "grinding" eliminates the monolithic shape of the component, thereby worsening leaching performance.

Waste disposal regulations are very strict. It is generally known that some of the traditional building materials like granite an Portland cement, if submitted to the same leaching or radiation tests as those prescribed for wastes, would be classified as dangerous (PERA, 1996). One reasonable alternative is to compare the traditionally used product with the new product-containing residue in terms of leaching. If the new product leaching results are inferior to the traditional product, the technology can be accepted. The Dutch Building Materials Decree goes a little further by stating leaching limits for all building materials. Above certain limits, a building material can be used only if it is protected from water. Moreover, after the end of the material's service life, disposal must be strictly controlled (VAN DER POEL, 1997).

Applying the LCA methodology as prescribed does not demonstrate all the benefits of recycling because it does not take into account the environmental benefit that arises from not depositing the waste in a landfill. This aspect deserves further discussion.

2.6. Technological transference

"Recycling only occurs when these new materials are incorporated into products that enter commerce" (SKINNER, 1994). Then, it is not enough to just develop new technologies but it is necessary to try to put then on to the market. From this point of view, technological transference is an essential part of the process.

There are plenty of technically excellent recycling technologies, which have not succeeded on the market. Even nowadays, in most countries, fly ash (CLARKE, 1994) and blast furnace slag are not entirely recycled, despite the fact that they have been on the market for 50 and almost 100 years respectively. Probably no other wastes have received as much scientific attention or had its technical and environmental advantages so well demonstrated.

Despite the technical and environmental excellence of a new material, its industrial production must be viable from different aspects.

The concept of *by-product synergy* proposed by the EPA and The Business Council for Sustainable Development - Gulf of Mexico (BCSD-GM, 1997) suggests that marketing successful recycling can be more readily achieved by collaboration, motivation, communication, innovation, participation, and evaluation.

Collaboration must involve all interested parties: waste producers, potential waste consumers, governmental agencies, community organisations, and the authors suggest, research institutions. One important aspect is the commitment of the waste producer to the recycling process, starting with the research and development phase. As emphasised by SKINNER (1994), the waste manager has to operate in a business like manner as a raw material supplier. It means that the culture of the company has to change. If the raw material supplier does not inspire confidence, it will be very difficult to find an entrepreneur interested in producing the new material. Governmental agencies have the legal power to halt any recycling process and they must be involved too. Community organisations also have the power to stop the process but they can help promote the new technology.

Collaboration also means that the research and development projects must be collaborative. The Brazilian steel industry is developing joint research projects with universities and other business companies to improve the recycling of blast furnace slag. Some waste companies even turn their waste product business into a new company, most of the time in a partnership with another company. British East Coast Slag Products is a joint venture of British Steel and Tarmac, a building related conglomerate.

3. CONCLUSION

Recycling waste as useful materials is a very important environmental management tool for achieving sustainable development. On the other hand, recycling waste without properly based scientific research and development can result in environmental problems greater than the waste itself.

The successful research and development of a new building material or component using waste as raw material, is a very complex and multidisciplinary task, including technical, environmental, financial, marketing, legal and social aspects.

Due to increasing concern in the business community about sustainable development in general, and in recycling in particular, it is possible to anticipate a growing number of research and development projects. In this business-like approach, recycling projects will be based on collaboration between different institutions.

The proposed methodology, properly developed can be a very useful tool for helping multidisciplinary teams to communicate and detect aspects where more basic research is needed.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

A laboratory experimental set-up for the study of organic compounds transport through unsaturated soils

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The presence of pollutants in soils is one of the major problems for the use of the groundwater and also for future use of the land. The contamination from reactive pollutants can derive from use of fertiliser in agriculture, from industrial processes as well as from illegal landfill. The remediation of these sites is still an open problem due to the different opinion of scientists, and to the different technologies now available on the environmental market. One of the main reason for the uncertainties in the correct choice of the remediation technique is surely that the behaviour of transport and dispersion of pollutants in soil is still not well known. Particularly, the adsorption/desorption phenomena are strictly related to the specific soil and to the specific contaminant. So it can be worth carrying out laboratory experiments (with low costs and with controlled conditions) to evaluate the parameters suitable for the understanding of the involved processes and for the eventual use of models. In the present paper an experimental study of phenol transport and dispersion in soil is proposed. It can be considered as a test on the suitability of laboratory reconstruction of a real situation. The aim is to build a low costs methodology that can give information in controlled situations on the soil response to a contamination. A careful research of sampling instrumentation has enabled us to build a test section larger than those generally described in the literature, in this way it was possible to have a heterogeneous and realistic soil structure . This last aspect can be considered as a step towards "in situ" conditions. A tracer is used to characterise the fluidodynamic part and a solution containing phenol is added to the soil. The aim is to reproduce the circumstances where contaminants in the upper part of the soil are transported by rainfall and add to the pollutant in the deeper part. The soil is completely characterised from the physical and chemical point of view. A soil moisture meter is used to evaluate the wet front in time and space and a tensiometer furnishes the value of the matrix potential in the section. A series of nine micro-lysimeters are used to sample to solution in time.

1. INTRODUCTION

Information on pathways of water flow and solute transport through the unsaturated zone is of importance in understanding and predicting movement and impacts of pollutants in small and large areas. Pollutants sources can be identified in unauthorised landfills, large use of fertiliser in agriculture and from accidental events by which toxic substances can be spread on the land. To this end numerous environmental fate and transport models have been developed (Nielsen et al., 1986; Van Genuchten and Shouse, 1989). Even if the most important processes concerning the flow and the transport can be considered known for a long time (Richards, 1931; Bear, 1972,),one principal limiting factor to model development is the lack of experimental research that examines transport mechanisms through unsaturated field soils (Dagan, 1986; Jury and Flubler, 1992).

Different experimental studies have been carried out in the past: Tindall et al (1995) developed an experimental apparatus to observe the nitrate leaching, using a tensiometer, suction lysimeters with a diameter of 1.5 cm and sets of TDR (Time Domain Refrectometry) to analyse the water content; a gas sampler completes the experimental apparatus. The test section was rather too large to assure the approximation of the physical and chemical properties of the field soil. Mishra and Misra (1990) analyzed the kinetic of the nitrification process in the soil using columns of 9cm x 8cm. Buther et al. (1995) completed a study on a soil composed of fractured rocks to evaluate the effects of the flow heterogeneity on the solute transport. Chloride was used as tracer. Maciojewsk (1993) used radiometric methods to study water and contaminant transport in soil. Shimjima and Sharma (1994) carried out laboratory experiments to study the transport of some chemical compounds in an unsaturated soil with different flow conditions. The column used as test section was high and narrow (100 cm x 10 cm).

The aim of this paper is to give a contribution to research in this field by reporting the experimental results of a study on a test section of soil under controlled conditions.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1 Soil

The soil used in the experiments was collected at a site near Rome experiencing ground-water contamination from agricultural use. The soil was utilised for packing one soil column 60 cm long and 44 cm diameter after sieving at 2 mm.

Analysis carried out on the sample furnished a composition mainly subdivided in 50.9 % clay, 45.1% silt and 4% sand. According to this the soil can be classified as a silty clay using the well known classification system (Hillel, 1982).Other information on the soil sample are of density $\rho_s = 2.6267$ g/cm^3, bulk density $\rho_b = 1.75$ g/cm^3, porosity f= 33% and residual volumetric water content $\theta_r = 0.13$ cm^3/cm^3.

The chemical analysis carried out on the soil gave a content of organic carbon TOC = 0.95 ±0.1% and of total carbon TC = 1.017 ±0.2%; the value determined for the pH was 6 and the CEC (cationic exchange capacity) was 31.01 meq/100g of soil. Chloride was employed as tracer. The initial content of chloride in the soil was estimated by ion chromatography and found to be 0.0169 mg/g.

2.2 Experimental apparatus

The column (60 cm long and 44 cm in diameter) was constructed of plastic materials. In the bottom of the column was positioned a drainage system made up of an upper layer of sand and a lower layer of gravel, the layers divided by a stainless steel micro mesh to prevent sand particles being dragged out by effluent.

The water content was measured by 9 soil moisture blocks made up of a metallic cage with gypsum. Two cables, connected to each block, were connected at one end to the soil moisture meter device used to obtain a measurement of the soil resistance in ohms. Volumetric water content of the soil was calculated from the calibrating shape obtained using the gravimetric method and the TDR apparatus. The blocks were located at three different level (10, 25 and 40 cm) from the top. At the bottom of the column there was an effluent collection device. One tensiometer was located 25 cm deep at the middle of the section.

Three soil solution samplers (suction lysimeters) were located in the soil column at the same level of the blocks. The following sections refer to the lysimeters as CL (10 cm from the surface), BL (25 cm), AL (40 cm) and with 1, 2, 3, with respect to the column location in the test section. The Rhizon soil solution sampler is a disposable sampler that consist of a tube made of porous polymer (diameter only 2.5 x 1.4 mm) connected to a PVC tube and a connector for the connection to a syringe. The porous material is reinforced by a stainless steel wire. The lysimeters were placed horizontally in the moist soil.

The leaching solution was sprayed evenly over the surface of the core with a vaporiser, connected to a submerged pump.

Figure 1 shows the experimental apparatus used in the experiments.

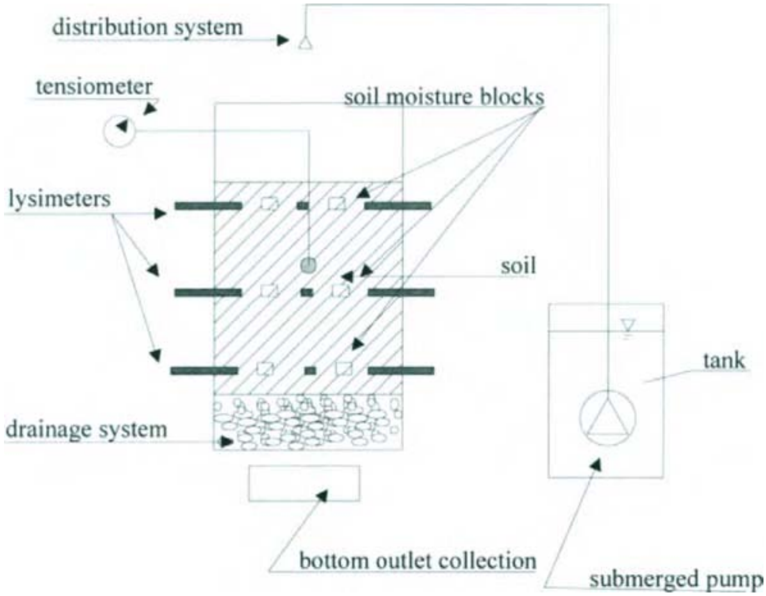

Fig. 1 Experimental apparatus

2.3 Experimental results

Three different programmes were carried out. The first was dedicated to the study of the water front advance, the second and third were performed feeding the column with chloride and phenol.

In the first experiment, the container, in which was the submerged pump, was filled up with 100 litre distilled water and 3g NaCl to immobilise the colloids. The rain was simulated twice a day for some minutes. Volumetric water content and suction were measured each time the rain was simulated.

Table 1 summarises the total volumes of water applied. Evaporation rate was negligible due to the fact that the experiment was carried out in a closed laboratory with humidity and temperature controlled.

The experiment was considered terminated 9 days after the first application of distilled water, when water flowed from the outlet of the column.

In figure 2 the trend of the water front is shown for one of the three columns.

Table 1 Total volumes of water applied

DATE	**Time**	**Application Time (min)**	**Flow (ml/min)**
21/01999	13:55	5	220
	17:40	5	220
22/01/1999	9:55	5	220
	16:30	5	220
23/01/1999	11:20	5	220
25/01/1999	10:25	6	220
	16:25	6	220
26/01/1999	10:35	6	275
	17:10	6	275
27/01/1999	9:35	6	265
	17:45	6	265
28/01/1999	10:20	6	260
	16:35	6	270
29/01/1999	9:45	6	280

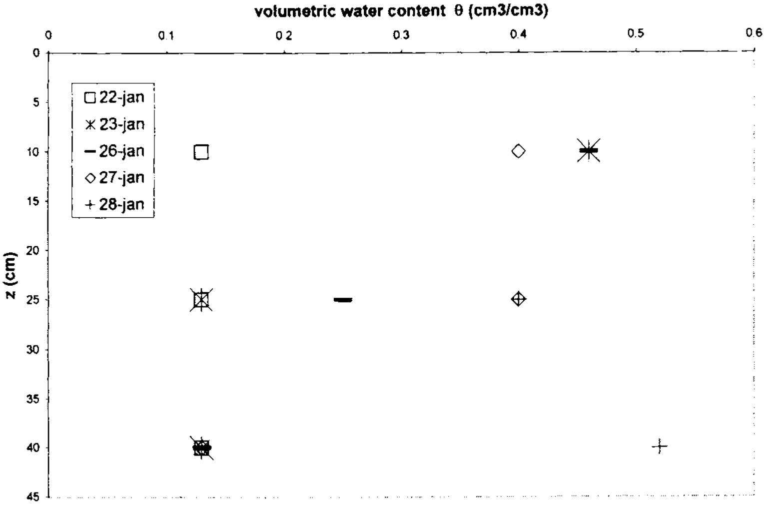

Fig. 2 Water content measurements

The water balance was computed, knowing the amount applied, measuring the water at the outlet and evaluating the water present in the soil from the measured humidity values.

At the beginning of the second experiment, 1g of phenol and 50 mg of chlorides dissolved in 0.5 litre distilled water was applied to the core, followed immediately by an application of 2.25 litres of distilled water. The solution was sprayed evenly over the surface of the core. After the first application, the soil column was watered twice a day with 2-2.8 litres distilled water (each time) sprayed evenly over the surface to simulate the irrigation or rain.

Water collected at the outflow flask was about equal to the water application rate and the volumes for the three samples extracted from the suction lysimeters from each depth ranged from 2-10 ml per sampling. Water samples were collected twice a day both from the bottom column and the soil solution samplers. Collected samples were frozen for future phenol and chlorides analysis.

The phenol concentration was measured by HPLC (High performance liquid chromatography), and the chloride by ion chromatography.

After the second experiment, the core was flushed with one volume of distilled water before the next experiment to displace any remaining soil C_6H_5OH and Cl^-.

In the last experiment 12 g phenol and 300 mg chloride dissolved in 3 l of distilled water were applied to the soil.

3. CHLORIDE AND PHENOL APPLICATION

1 g of phenol and 50 mg of chloride in half litre of distilled water was used as contaminant application in the second run. 4765 ml of water were applied with a constant flow rate of 34 ml/min by 16 applications in 9 days.

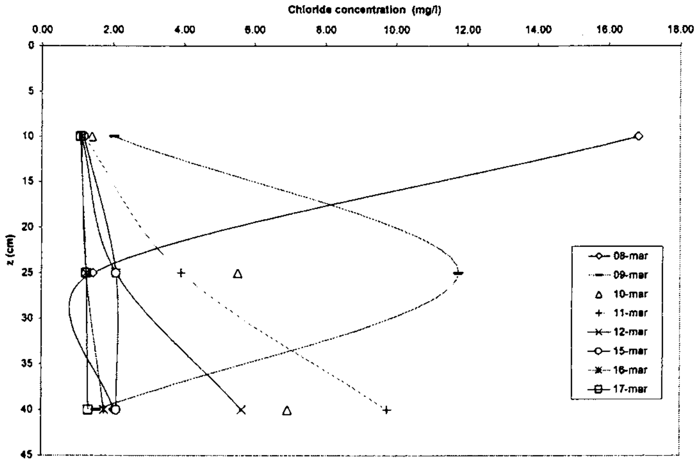

Fig. 3 Vertical distribution of chloride in column 3

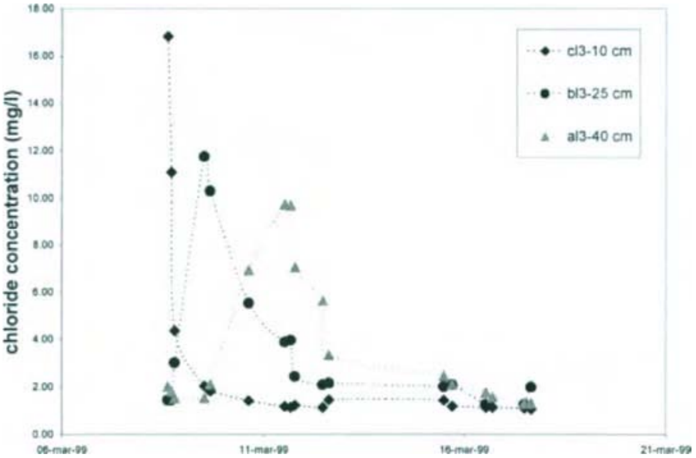

Fig. 4 Chloride concentration vs. time in the three lysimeters (column 3)

Figures 3 and 4 show examples of experimental curves obtained during the first series for chloride (second experimental series). Figure 3 shows the vertical distribution of the concentration, while figure 4 shows the measured concentration values vs. time in the three lysimeters of column no. 3.

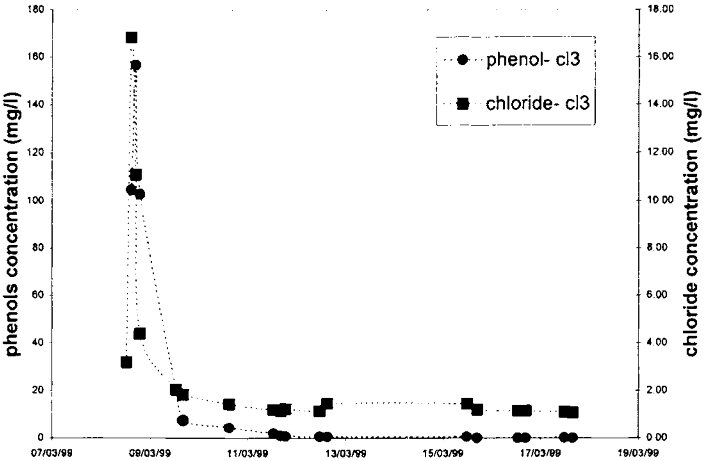

Fig. 5 Comparison between chloride and phenol measured values (column 3)

Figure 5 compares the measured values of chloride and phenol vs. time in column 3 in the upper lysimeter. It is possible to observe a small retardation of the phenol front. The curves are indicative to the first layer because in the deeper lysimeters the analysis has always furnished a concentration of the phenol equal to zero. This result was probably due to a fast degradation of the phenol by the bacteria In the upper layer the oxygen needed for the aerobic degradation of phenol was not a limiting factor, thereby allowing a fast degradation of the readily degradable phenol.

In the third series 12 g of phenol and 300 mg of chloride dissolved in 3 litres of distilled water were applied. 4480 ml of water were successively applied for 164 minutes with an average flow of 27.3 ml/min for 9 days.

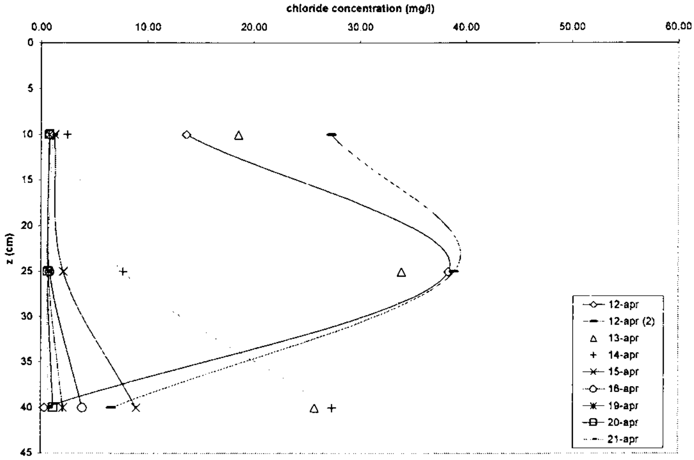

Fig. 6 Evolution of the vertical distribution of chloride in column 3

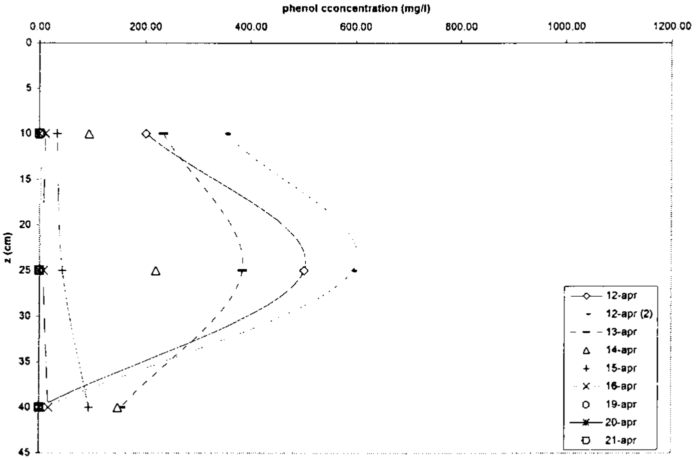

Fig. 7 Evolution of the vertical distribution of phenol in column 3

Figures 6 and 7 show the vertical profile of the chloride and phenol concentration in time. Due to the higher phenol concentration its degradation was probably reduced by a concentration inhibition effect, allowing a clear identification of phenol migration.

4. CONCLUSIONS

The experimental set-up presented has demonstrated its suitability to study contaminant transport in an unsaturated soil. The controlled conditions and the large number of samples collected can be used to analyse the phenomena occurring in the transport process in the soil. The larger dimensions of the test section can reproduce the heterogenities which characterise real soils. Furthermore the study has given a large set of data which can be used for calibration of reactive chemicals transport models in unsaturated soils.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Sustainable ash pond development in India
-a resource for forestry and agriculture-

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In India, the annual production of coal fly ash is approximately of the order of 70 million tons per year. Most of the production is stored in large ash ponds. Current waste disposal regulations call for the retired ash ponds to be covered with a top soil to prevent leaching of contaminants and erosion of fly ash into the surrounding environment. However, absolute containment of ash ponds on the longer term in a tropical climate is far from feasible: the covering on these ponds dries out and cracks. In addition, the topsoil is stripped off from other fertile areas, away from the site.

Our present understanding of coal fly ash leaching in a disposal environment has largely obtained from freshly, unreacted ashes and not from ashes, which have been allowed to weather in the open. We showed in a previous paper that alkaline fly ash weathers relatively rapidly into soil-like material when disposed in the open. In this paper, it is argued that fly ash analogous to volcanic ash, has a high potential for large-scale utilisation in forestry and agriculture. A new concept of sustainable ash disposal and utilisation in India is presented.

KEYWORDS: alkaline coal fly ash, ash disposal, fly ash management, weathering, clay formation, volcanic ash, forestry

1. INTRODUCTION

Coal is second to oil as a primary energy resource and fly ash is the main solid byproduct of coal combustion (10-40 % w/w). Over the next 15 years, world coal use is expected to increase more than 2 percent annually. Growth in China and India alone will account for more than 60 percent of this incremental coal demand and 40 percent of world coal use projected for 2010 [1].

In Asia most of the fly ash (e.g. ~ 5 x 10^7 tons/year in India alone) is stored in large ash ponds. Because fly ash contains elevated levels of leachable salts and heavy metals, disposal of such huge quantities raises serious environmental concerns [2]. In India current regulations call for the retired ash ponds to be covered with a top soil to prevent leaching of contaminants and erosion of fly ash into the surrounding environment. However, absolute containment of ash ponds in the longer term in a tropical climate is impossible: the covering on these ponds dries out and cracks. In addition, the topsoil is taken from other fertile areas, away from the site.

In India, the construction of large ash ponds results in resettlement issues and loss of crop production, farmland and natural habitat. For each megawatt of electricity produced from coal 0.1 ha. of land is required for ash disposal [2]. The total ash pond area in use in India is about 20.000 ha. The total area required for disposal in the next 20 years is expected to increase to about 40.000 ha. In order to minimize the environmental and economical damage of unsustainable ash disposal there is currently no strategy for engineering and management of ash disposal systems in India. Besides disposal, a small part of the Indian ash production is used in building materials. However, due to economic constraints it is expected that only a very limited portion of the total Indian fly ash volume is expected to be utilized in this way in the near future.

Recently, we studied the weathering of Indian coal fly ash derived from an open disposal site and compared it with published data from weathered volcanic ash, its closest natural analogue [3]. Both types of ash contain abundant aluminosilicate glass which alters to non-crystalline clay. However, the kinetics of coal fly ash weathering appeared to be much more rapid than those of volcanic ash because the higher pH of fresh coal fly ash promotes rapid dissolution of the glass. After about 10 years of weathering the non-crystalline clay content of the studied ashes was higher than that of 250 year-old volcanic ash. We observed that upon weathering, heavy metals which were mobilized during dissolution of glass and other minerals, were immobilized by this non-crystalline clay and ferrihydrite. The observed rapid clay formation together with heavy metal fixation imply that the long-term environmental impact of coal fly ash disposal may be less severe than predicted from previous studies on unweathered ash. Based on these findings we argued that isolating coal fly ash from the weathering cycle may be counter-productive because in the long-term under conditions of free drainage fly ash is converted into a soil-like material capable of supporting agriculture. The ideal situation would aim for leakage at a rate and concentration which can be accommodated by the local environment. After completion of this 'natural' detoxification process the ash can be used for cultivation projects i.e. crop production, farm land, or afforestation.

In considering the potentials of establishing forestry and crops on weathered ash deposits, it is mandatory to obtain information on the behaviour of constituents in the ash, which are likely to be injurious to plants, as it weathers. Ash properties which are known to be detrimental to plant growth are [4]: (i) high salt content, high alkalinity, high levels of available boron, (ii) the lack of a normal soil micro-biology, and (iii) low levels of available phosphorus and nitrogen. In this study particular attention is paid to the rate of chemical change of the constituents which are injurious to plants. It is argued that fly ash analogous to volcanic ash, has the potential for large-scale utilisation in forestry and agriculture. A new concept of sustainable ash disposal and utilisation in India is presented.

2. MATERIALS AND METHODS

2.1. Site

This study was conducted at a temporary ash pond near the ash disposal facility of Ramagundam Super Thermal Power Station (RSTPS), located in the Karimnagar District of Andhra Pradesh, India. Directly after deposition in 1986, the site was planted with trees (*Acacia auriculiformis, Casuarina equisetifolia, and Eucalyptus globulus*). The annual rainfall in the Karimnagar District is 1,100 mm. Most of the rainfall (75%) is received in June, July, and August. Mean temperatures in the summer and winter season are 42-30°C and 30-15°C, respectively. Only in the wet season the ash in the ponds becomes saturated and the rainfall promotes rapid and intense leaching. The thickness of the ash layer in the forestry plantation was approximately 4 m. The total area was approximately 1 ha.

2.2. Sampling and analysis

After 8 years of weathering, samples have been taken from the ash layer at different depth for total element analysis, Cation Exchange Capacity (CEC), pH and conductivity (EC) determination and shaking tests. Shaking test (L/S= 5, t=24 hr) with demineralized water were conducted to determine the leachablility of salts (e.g. sodium and sulfate), boron, molybdenum, and chromium.

3. RESULTS

At the time of sampling the trees were showing excellent growth. Moreover, the ash was covered by a luxuriance of natural vegetation (see Fig. 1). In Figure 2 pH, EC, CEC, total concentration of Na and SO_4, and total and leachable concentration of Cr, Mo and B as a function of depth are given. The ash layer consists of friable, dark greyish brown silty ash in the first 0.05 m followed by light greyish, weakly cemented ash in the lower profile. The surface layer is enriched with visible partly decomposed organic material. Fine biopores and roots are observed throughout the entire profile becoming less common at a depth of more than 1 m. At a depth of 1.3 to 1.6 m much coarser and darker ash is found. The ash layer at this depth is likely to consist predominantly of bottom ash. In the lowest part of the ash profile (from 3.60 m) the ash is completely saturated, sticky and plastic. The CEC values of the weathered ash are significantly higher than that of the original unweathered ash, which has an average value of 2.9 $\mathrm{cmol_c kg^{-1}}$ [5]. Highest CEC values are found in the upper layer of the ash profile, where weathering is most intense and organic matter is accumulating.

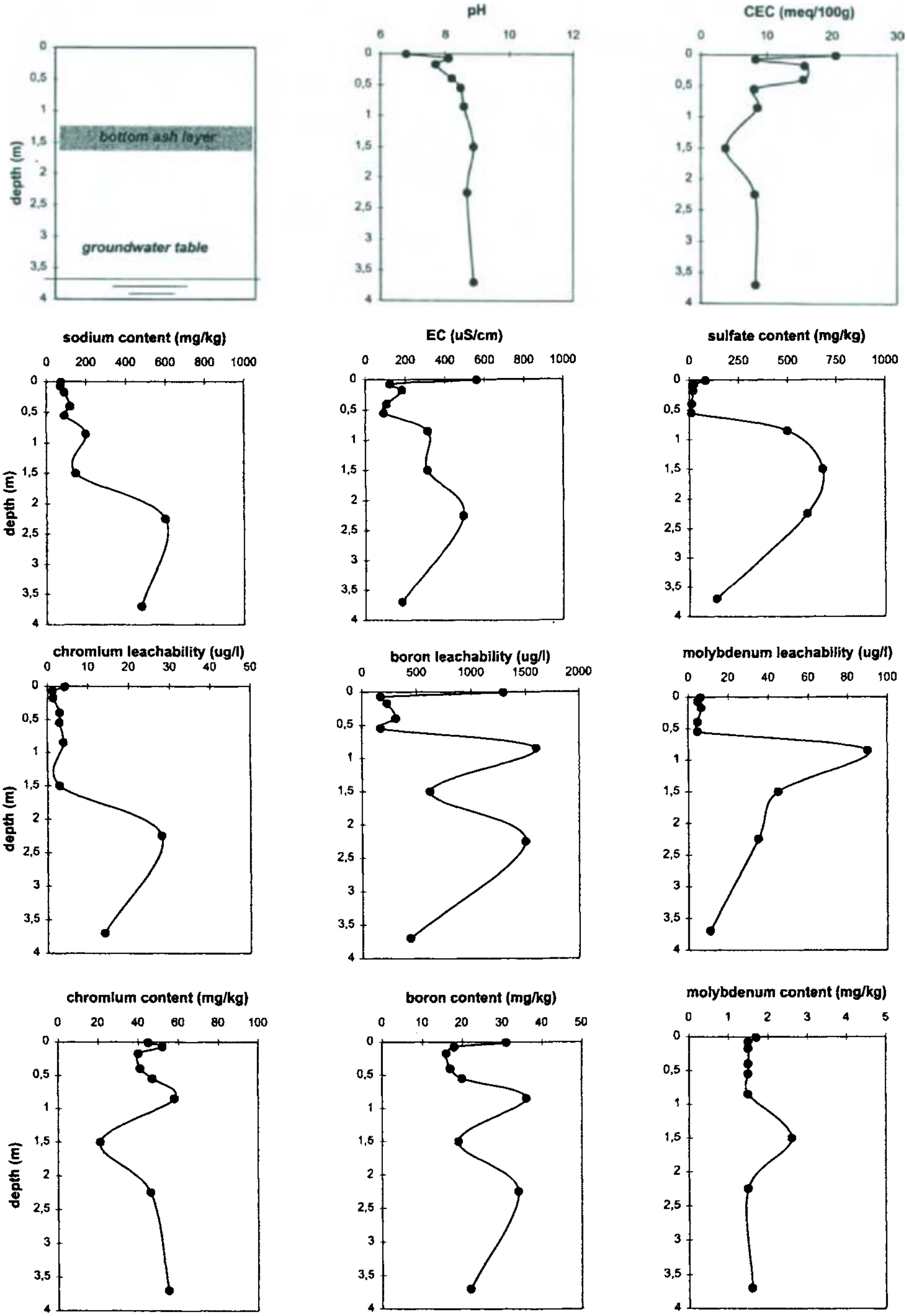
In the organic rich top layer the pH attains a value of 6.8. Below the top layer the pH slightly increases with depth from pH values of 8.0 to 8.6, which coincides with the generally observed pH of ash leachates in equilibrium with atmospheric CO_2 [6]. Hence, even in the lowest, saturated part of the ash profile neutralization of the initially alkaline fly ash by CO_2 has been accomplished. The curve of the total content of Na and that of the leachability of Cr exhibit a very similar pattern, which indicates that the leachability of Cr is determined by its availability rather than by sorption and/or precipitation processes. This implies that Cr is

Figure 1. Study area (forestry plantation on fly ash in Ramagundam, India (8 years old))

very mobile under the prevailing initial weathering conditions. As a consequence, the labile Cr fraction has been washed out almost completely in the upper ash layer up to a depth of appr. 2.0 m after 8 years of weathering. By contrast to the labile elements, SO_4, Mo and B exhibit a different behaviour. The mobility of these three constituents is much lower which indicates that the displacement of these (oxy)anions in the ash profile is controlled by sorption and/or precipitation. These constituents become less rapidly depleted in the upper layer. Comparison of the total and available fraction reveals that boron is relatively resistant to leaching. An indication that this element is predominately present in the glassy structures of the ash. The observed surface enrichment of B is likely due to the affinity of boron to bind with organic matter. Boron is a toxic element to many plants species when present in soil solution in concentrations only slightly greater than the optimal concentration required for plant nutrition [8]. Water soluble B between 1 to 5 ppm in soils usually allow normal growth of plants, whereas levels higher that 5 ppm water soluble B may supply toxic quantities of B. Hence, the observed leachable B concentration in the subsurface layer is expected to be too low to be detrimental to plants.

After 8 years SO_4 and Mo become depleted in the upper layer (up to 0.5 m). The maximum availability of SO_4 at a depth between 1 and 2 m coincides with the maximum availability of Mo. The displacement of SO_4 in the lower ash profile is likely controlled by the solubility of gypsum ($CaSO_4.2H_2O$) and that of Mo by the solubility of $CaMoO_4$ and/or sorption on amorphous aluminosilicate hydrates and/or Fe(hydr.)oxides [9, 10]. The observed relatively low availability of all the investigated constituents in the saturated bottom layer is likely due to (horizontal) convective ground water transport.

Figure 2. pH, EC, CEC, total concentration of Na and SO_4 and total and leachable concentration of Cr, Mo, and B as a function of depth.



In conclusion, in open ash deposits the chemistry of the pore water will progress from one with a high pH, and relatively high salt, Cr and Mo concentration to another with moderate pH and low salt and metal concentration. Our observations also reveal that B injurious to plant growth fall rapidly from relatively high levels to that of a normal soil. It is important to note here that as a result of the extreme seaonality of the rainfall and the relatively high average temperatures, the intensity of weathering may strongly contrasts with that in temperate climates.

4. SUSTAINABLE ASH DISPOSAL

Leaching of contaminants from alkaline coal fly ash is inevitable both in an open and a closed disposal system. However, in a closed disposal system the time scale in which leaching occurs is unpredictable. By contrast, in an open disposal system leaching can be controlled within a time scale amenable to monitoring and resource management depending on the ash properties, disposal height and prevailing hydrological and climatological condition. Based on these findings, a new and sustainable concept of ash disposal for land development has been developed. In this concept natural weathering processes are exploited to (i) control leakage of leachate at a rate and concentration which can be accommodated by the local environment and (ii) convert the ash into a fertile soil over a manageable period.

The principle objective of the concept is to provide an environmental and economical sustainable solution for a significant fraction of the ash production in India (and in other ash producing developing countries (e.g. China)).This objective is achieved by:

1. Detoxification and improving the agronomic properties of the fly ash during disposal;
2. Restoration of the land used for fly ash disposal to its original level or even to a higher level of productivity within a manageable period.

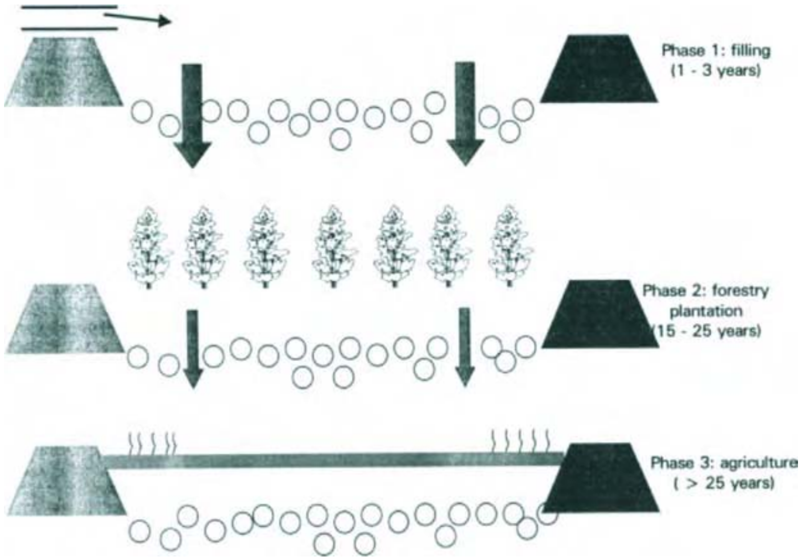
Phase I

In the first phase the ash is stored into small compartments up to a height of 1 to 3 m. During this filling phase, which will last 1 to 3 years depending on the ash production rate and the surface area of the compartment, weathering and leaching cause a rapid reduction of the salt concentration in the upper horizon of the ash layer to harmless levels. Simultaneously, weathering also imposes a rapid reduction in the (bio)availability of heavy metals. The rate of discharge of salts and heavy metals is determined by the ability of the receiving environment to accommodate these pollutants, without detriment to the uses specified for the waters (surface and/or groundwater) concerned. Operation in small compartments allows control of the rate of discharge from the ash and is, therefore, considered as the best feasible method to mitigate groundwater contamination from ash pond leachate. Moreover, the advantage of storage of the ash in small compartments instead of in one large settling pond is that plantation can commence considerable earlier than at the end of the lifetime of the power plant, which is at least 25-30 years.

Phase II

Following the first phase, a forestry on the ash compartments is established in the second phase by tree planting, and depending on the selected tree species, by adding fertilisers. The

The concept comprises three consecutive phases of operation as illustrated below.



plantation further enhances the weathering process and neutralization of the pH and the agronomic properties of the ash through the generation of organic matter. During this weathering process the available concentrations of constituents injurious to plant growth (e.g. boron) decreases to a level approaching that of a normal soil. The time required to reach this stage depends on the local climatic conditions and is estimated in India at a maximum of 20 years.

Phase III

Finally, in the third phase, the detoxified and fertile ash will be used for agriculture. We infer that the agronomic properties will be very similar to those of the highly fertile soils (Andosols) derived from volcanic ash. and that the fertile ash will not impose any risks of introducing bio-accumulative contaminants in the food chain.

5. CONCLUDING REMARKS

Based on this study and previous work of the authors the following conclusions can be drawn with respect to the investigated Indian, alkaline fly ash:

- a plant cover and/or forestry can be developed directly on the fly ash after filling the pond and without amendment with fertilizers;
- under conditions of free drainage weathering processes reduce the availability of contaminants by depletion and/or chemical fixation, and thus result in a detoxification of the ash pond;

- along similar lines as volcanic ash, in the longer term, depending on the prevailing local hydrological and climatological conditions, a fertile soil will develop from the vegetated ash.

These findings substantiate that isolating coal fly ash from the weathering cycle may be counter-productive, because in the long-term under conditions of free drainage fly ash is converted into fertile soil capable of supporting agriculture. If implemented appropriately, the concept of open ash disposal is anticipated to have very strong environmental and economic benefits.

ACKNOWLEDGEMENT

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Behaviour of cement-treated MSWI bottom ash

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MSWI bottom ash is the residue of combustion. The use of bottom ash in road construction is wide spread. French legislation forbids the disposal of reusable waste in special landfill from 2002. Moreover, " arrêté du 9 mai 1994 " provides environmental criteria (leaching threshold, etc), and evaluates this material according to utilisation in road construction. In such applications, bottom ash is often treated with binder to improve its mechanical features. Nevertheless, bottom ash is subject to chemical problems. These problems induce an expansion, which brings about cracking and finally road destruction. Therefore, it is necessary to estimate the swelling potential of MSWI bottom ash prior utilisation. This is one of the aim of the European contract " Mashroad "(contract BRST CT97-5150).

This study involved four years of work on cement treated MSWI bottom ash. It examined different tests that show the importance of oxidation of aluminium in the swelling reaction and the efficiency of different treatments. Different binders were used in order to have different proportions of clinker. The kinetic aspects of aluminium-binder reaction were also studied. Finally, we present a special cell to measure the swelling pressure of these materials.

1.INTRODUCTION

The production of municipal wastes in the European community is estimated at about 150 million tons per year. Today, only 20% is incinerated which represents about 9 million of tons of municipal solid waste incinerator (MSWI)ash. This is principally disposed of in landfill. These quantities will increase considerably with the growth of municipal waste production, the progressive closing of landfill, the definition of new environmental standards, and reuse and elimination policies.

In France, the environmental policies [1] accept the utilisation of small leaching part MSWI in road construction. The parts of MSW which are incinerated are about 40%. The utilisation of treated or untreated MSWI ash is limited essentially in applications like embankments in road construction or buildings far from water sources.

The respect of environmental rules is not the only criterion for utilisation. The geotechnical aspect must be addressed. In fact, bottom ash is subject to chemical problems that induce expansion and pavement cracking. The aim of this study is to deal with this problem of expansion. This work approaches different points:

- the study of MSWI ash behaviour,

- the measurement of expansion,
- the impact of treatment with binders on expansion,
- understanding of the chemical reactions that result in swelling.

This study began in 1996 and is now the subject of the European project MASHROAD (BRST-CT97-5150).

2. MATERIAL PROPERTIES

The MSWI bottom ash studied comes from Lagny sur Marne where the company Yprema is sited. Yprema prepares the material for direct use in road construction. The different steps are:

- to sieve to a size distribution about 0/31.5mm,
- to remove iron particles,
- to age the MSWI bottom ash for more than 2 months.

The size distribution is given in Figure 1. This curve qualifies the ash for direct utilisation, after an aging period, in road construction. The MSWI bottom ash is frequently treated on the platform for an embankment or road utilisation.

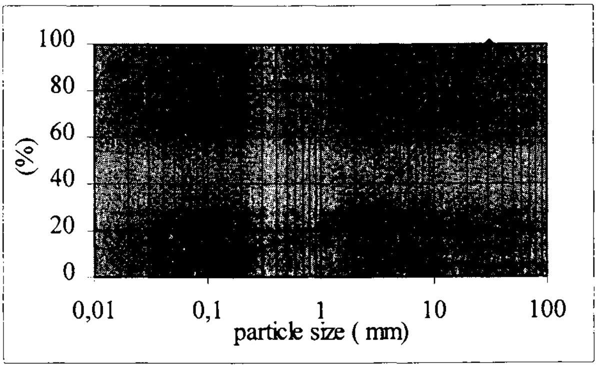

Figure 1 - Particle size distribution

The mineralogical composition is presented in Figure 2. The MSWI bottom ash used in this study is classified in the V(for the French valorisation) category so, the environmental aspects are not considered further in this paper.

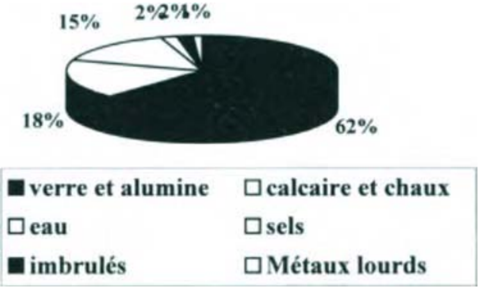

Figure 2 - Mineralogical composition of MSWI bottom ash

3. MSWI BOTTOM ASH EXPANSION

As mentioned earlier, bottom ash may show chemical reactivity, which is responsible for expansion and may bring about cracking and finally road destruction. In order to pursue utilisation of the material in road construction, our understanding of reactions that lead to bottom ash deformation must be improved. Many causes of expansion were postulated. Here, after presenting the different causes, the occurrence of each of the reaction products is examined. In order to do this, bottom ash samples were placed under several conditions which lead to these different kinds of swelling.

3.1. Causes of Swelling

Previous studies show different causes of swelling, and conditions which lead to these phenomena. Three main reasons are well known :

- formation of gel from oxidation of metallic aluminium.

At high pH (> 10), the metal is dissolved, with emission of hydrogen.

$$\begin{array}{l} 4Al + 16OH^- \rightarrow 4Al_2O^- + 8OH^- + 12e^- \\ \underline{12H_2O + 12e^- \rightarrow 6H_2 + 12OH^-} \\ 4Al + 4OH^- + 4H_2O \rightarrow 6H_2 + 4AlO_2^- \end{array}$$

This reaction can occur when there is contact between metal and water or OH^- ions. However iron reduction could end up in the same result. In fact, many studies showed expansion near iron particles [2]. When the pH goes down to 9 – 10, aluminium hydroxide forms a $Al(OH)_3$ gel:

$$AlO_2^- + 2H_2O \rightarrow Al(OH)_3 + OH^-$$

- ettringite formation

This reaction takes place when the material is saturated with water [3].

$$Al_2O_3 + 3CaSO_4 + \underset{\text{lime}}{3Ca(OH)_2} + 28H_2O \rightarrow \underset{\text{ettringite}}{(CaO)_2(Al_2O_3)(CaSO_4)_3(H_2O)_{31}}$$

- lime and magnesium oxide hydration

The Free calcium oxide and magnesium oxide cause instability by their transformation into hydroxide.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$MgO + H_2O \rightarrow Mg(OH)_2$$

The resulting expansion appears less important than the two others mechanisms. Each sort of swelling could happen depending on the bottom ash treatment history.

3.2. Experimental program

The aim of the experimental work was to look for each of the reaction products and to show the degree of swelling which was the outcome of the different reactions.

The test specimens were compacted bottom ash samples in CBR cylinders under a 4.5 kg load.

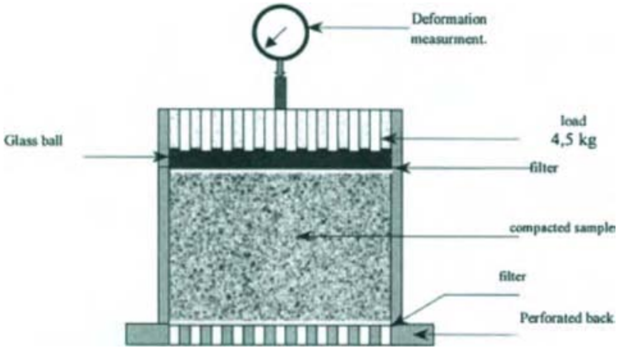

Figure 3 – sample in CBR cylinder

They were submitted to specific treatments which promote the different expansion reactions.

- Storage under wet conditions

The samples were kept in a wet place where oxygen and humidity foster expansion from aluminium oxidation.

- Storage under water at 40 °C

The aim of this test was to find proof of ettringite formation. Naturally, the formation of ettringite is a very slow event. Use of a higher temperature increased the reaction kinetic and allowed observation of the occurrence of this reaction in a shorter time.

- Storage under water at 80 °C

Under these conditions, expansion caused by calcium or magnesium oxide hydration could be observed. This test was based on a Belgian accelerated underwater test carried out at 70 °C on the LD slags [4].

The axial deformations of all samples were measured over several months.

3.3. Results

Figure 4 shows the expansion of bottom ash for each treatment history. The highest degree of swelling was observed under wet air conditions (2 %). The expansion of bottom ash samples kept underwater at 40 and 80 °C remained much lower (< 0.25 %).

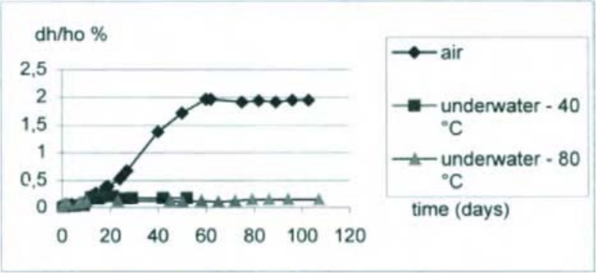

Figure 4 - MSWI bottom ash swelling under various conditions

3.4. Conclusions

Some uncertainty regarding the results of these tests remains: perhaps the testing time was too short to cause swelling due to ettringite formation or oxide hydration, despite the increase of temperature. However, the wet air atmosphere seemed to be the worst conditions for the bottom ash. Under these conditions, the greatest expansion was observed. Moreover, chemical analyses of the swelling gel confirmed the presence of $Al(OH)_3$.

Thus, it appears that the oxidation of metallic aluminium is the main cause of swelling.

4. ACTIONS OF BINDERS TREATMENT ON MSWI BEHAVIOUR

As it is very difficult to extract non ferrous metals from MSWI bottom ash on an industrial scale, one solution is to treat MSWI bottom ash with cements. Laboratory experiments were conducted to observe the impact of different cements on the swell. Different binders were used :

- an artificial Portland cement with low C_3A content(CPA),
- a mix of lime and slag.

A cement content of about 3% of the total weight was used. The differences between these two cements were :

-the pH which is more alkaline with the Portland cement,

-the hardening time which is faster in the case of Portland cement (about 6 hours).

These parameters are the most important with regards to oxidation of aluminium metal [5,6].

Table 1 presents the different compaction conditions. The reference is always the modified Proctor Optimum (OPM). The tests conditions are the same as those explained in part 2.

Table 1
Compaction characteristics

	dry density at OPM	OPM Water content (%)
No treatment	1.84	12.3
CPA	1.87	13
Lime and slag	1.85	14

Figure 5 presents the swell deformation vs time. One can observe that Portland cement treatment reduces the swell deformation about 70%. The slope of the curve is higher for this treatment than the other. This effect was attributed to the pH. The second part of the curves shows a competition between mechanical properties and swell deformations.

The swell deformation is principally due to oxidation of metals such as aluminium or iron. The photos present the products of this reaction. In Photo 2, the cracks induce by the swell can be observed.

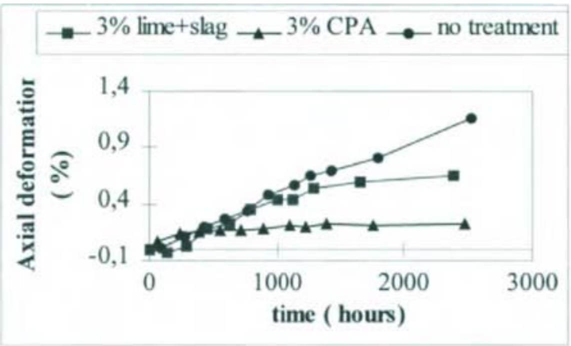

Figure 5 - axial swell deformation vs time

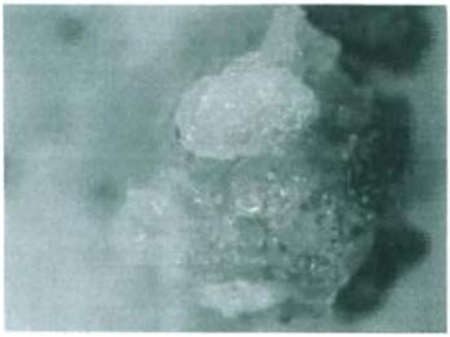

Photo 1 : Al(OH)3product of oxidation of aluminium metal.

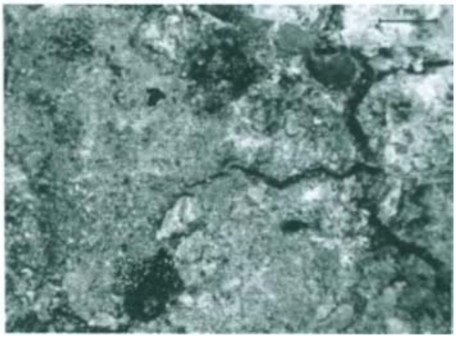

Photo 2 : Fe2O3 product of oxidation of iron.

5. CONCLUSION

These four years of research on MSWI bottom ash allowed us to quantify the influence of cement treatment on expansion. Moreover, it was possible to explain the origin of these expansions primarily as oxidation of aluminium metal.

In road design, the engineer needs a maximum swell stress rather than a maximum swell deformation. Work is continuing with the design of a new cell which measures the maximum stress of the swell reaction. In order to control oxidation and water content, unsaturated conditions based on in situ parameters are used.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

The re-utilisation of discarded building materials in cement-stabilised layers of road and airfield pavements

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Re-utilisation of marginal materials is standard practice in road and airfield pavement construction. However, not all marginal materials have sufficiently well known performance properties or, if they are known, are suitable for a generalised use.

For instance, Construction and Demolition (C&D) wastes are materials that can be used, in accordance with some specific rules, in the construction of road and airfield pavements. A study carried out by the University of Padua (Italy) has proved that these materials can be re-utilised in rigid pavements and has demonstrated the most useful options and criteria for optimising the results (Pasetto, Leeds, 1999).

Further research has confirmed the possibility of using C&D materials, as they are, as well as in cement bound or hydraulic-binder stabilised mixtures, in subgrades, sub-bases and road bases of flexible pavements.

Chemical, by means of leaching tests, and physical-mechanical characterisations by standard laboratory tests (compaction, CBR, freeze-thaw cycles; compression, tensile strength, secant and tangent elastic modulus, dynamic modulus using ultra-sound devices on different aged mixtures) have been done on discarded building materials of different origin and grading. It has been ascertained that if the recycled aggregate seems to be inferior to the natural one, if it is used in cement bound mixtures, it becomes equivalent to the traditional material or even preferable because it is cheaper and harmless to the environment.

1. INTRODUCTION

The boom in the civil and industrial building sector dates back to the beginning of the 20th century when the introduction of new materials (most importantly reinforced concrete) and technical innovations created the conditions for satisfying the demand for new buildings and infrastructures in a lively and rapidly expanding society.

Population increase, economic growth in the developed countries and the need for closer internal and external socio-political relations in the more advanced nations called for new commercial centres, more widespread residential and industrial areas and sites for the development of service industries. These all required the construction of major communication routes, infrastructures and services capable of satisfying the needs of modern society. At that time, the ample virgin spaces and the more or less unlimited resource availability (raw materials and financing) put no curb on huge new feats of engineering that were realised with few constraints for some decades, initially out of simple necessity and, later, as a consequence of wartime destruction.

Furthermore, buildings that began their useful life at the beginning of the century soon began to show needs of maintenance (sometimes even radical) that would soon also involve the many inadequately designed constructions, whose structural inadequacies suggested demolition and rebuilding in the light of more recent discoveries and new building techniques. The absence of a clear and precise planning policy in the building sector also meant the squandering of resources, aggravated by the constantly changing needs of a rapidly evolving society more interested in experimenting new ideas rather than converting existing structures.

The times of war in the 20th century would play an ambivalent role in all this. On the one hand they gave an inevitable new impulse to building activities, but on the other, attracted attention for the first time on the elevated social costs of upgrading existing structures, since many required demolition. This involved considerable costs of debris disposal and the no less relevant expense of procuring the resources for rebuilding.

More recently, the difficulty in finding low cost raw materials for construction (especially natural aggregates) that safeguard the environment, the increasing cost of eliminating discarded materials from all human activities (from civil demolitions, extraction activities, industrial and municipal wastes), the lack of areas for allocating these wastes and the environmental impact of existing dumps, have highlighted the lack of rationality that has inspired building activities in the past. The so-called waste materials could therefore play an important role in the building sector where, if they are recycled, they can be considered as raw materials, instead of just debris.

In fact the reuse of marginal materials coming from the demolition of civil engineering structures offers the following advantages:

1. saving of natural stone aggregate, the availability of which is decreasing due to the environmental damage produced by the extracting activities;
2. possibility of selecting natural stone aggregate only in the cases where the substitute material is shown to be not adequate or equal to the traditional raw material;
3. reduction in disposal costs of the debris, with less searching for storage space;
4. lower visual, chemical and atmospheric environmental impact of the debris.

The main problems linked to the re-use of marginal materials are instead:

1. the need to render the waste material suitable for use (improvement treatments, such as washing, sieving, selection, correction with or addition of a binder; specific design measures to improve the structural properties of the material);
2. the need for more assiduous controls of the quality of the non-conventional aggregate;
3. the need to take precautions for the protection and monitoring of the local environment;
4. increased maintenance of the structure built with the marginal material (for the same reasons as those in point 3);
5. the inevitable rise in the market prices of the high quality aggregate, because of the accompanying reduction in the quantities produced;
6. standards constraints.

Among the different types of waste, debris from the demolition of the civil engineering structures are one of the materials best suited to reuse, because, with the exception of some components (asbestos, varnishes, wood, plastic materials...), they are chemically inert and have, after suitable treatment, physical-mechanical properties that are equivalent to the natural aggregates. Amounts compatible with the needs of the building sector are now available. If the calculation is right that Italy will soon cross the threshold of 50 million cubic metres of material from demolition, this equals the current annual production of concrete.

In Austria, Germany, Belgium and the UK, demolition debris form construction material in current use, even for structural components. It has been reported [1] that since 1982, the A.S.T.M., 1986 the Dutch C.U.R, 1989 the Danish D.I.F., 1993 RILEM (TC 121) and at different times, the USA (U.S. Army Corps of Engineers), Japan (B.C.S.J.) and the Soviet Union, have all decided to regulate procedures for the use of recycled materials (equivalent to the natural materials) in the construction sector, both in building activities and especially in road and airport superstructures. It has also been demonstrated that exceptions no longer exist to their use, even in the surface layers of rigid and flexible pavements.

2. USE OF DEMOLITION MATERIALS IN ROAD AND AIRPORT INFRASTRUCTURES. EXPERIENCE INTERNATIONALLY

There have been many studies and applications with the aim of reusing aggregates made from material from the demolition of civil engineering structures in the construction of road infrastructures. A recent paper [1] discussed the results of a study, carried out at Padua University, to ascertain the suitability of the debris from civil demolitions in the construction of concrete paving slabs. The current paper intends to illustrate the results of a similar research project conducted on the same substitute materials, this time used as components of the load-bearing sub-bases of road and airport superstructures, and road embankments.

The study, conducted at the Construction and Transport Dept. of Padua University, was developed in accordance with international experiences referring to the different uses of Construction and Demolition (C&D) debris in terms of location and application methods.

For example, the PIARC (Permanent International Association of Road Congresses) [2] cites the use of degradable materials and debris containing cement mortar in embankments, while signalling potential correlated environmental problems, especially in relation to the position of groundwater. Demolition wastes coming from milled pavements or concrete and reinforced concrete are used, with or without stabilisation, in road bases; the reuse of stones and bricks from demolished buildings is reported for road bases and flexible wearing courses; the reuse of substitute materials within the ambits of the so-called "recycling" of road pavements is taken for granted.

On the subject of C&D debris, the PIARC states that the basic conditions for a profitable use of the substitute material are substantially the following: its availability in large quantities in relation to use (for the greatest economic benefit); the limited presence of pollutants (plastics, metals, wood) in the material from which it originates. With these conditions, the marginal aggregate can be used in sub-bases and road bases, sometimes stabilised with a hydraulic binder, even in heavily trafficked roads (France). Experiments in Austria are cited (mainly with stones and bricks from demolition) and Belgium (more or less with inert materials coming from the milling of bituminous courses with a low binder content: compare also [3]) in unbound sub-bases of road pavements. Some limited uses in Japan and Germany are reported (especially with pavement debris), where several tens of millions of tonnes per year of demolition materials are produced; it is also reported that in some regions of northern France almost all the demolished concrete is reused for sub-bases of superstructures. In Holland the reuse of demolition waste (concrete, masonry) is cited in road bases, in a climate both damp and temperate.

Most importantly, the PIARC shows that specifications and tests used for the characterisation of the marginal material are the same as those in common use for natural aggregates (grading, frost resistance, Proctor...). The only disadvantages the users of these products complain about are correlated to the possible heterogeneity of the aggregate supply (determined by the variability of the structural components demolished) and the increased sensitivity to water and frost. Regarding this, in Germany, the aggregate of C&D debris, utilised in embankments, sub-bases and road bases, is subject to rigorous controls according to the TP Min-StB standards (composition, impact strength, bad weather resistance, volume stability, water absorption, resistance to frost and thaw, shape index, cleanliness, density...).

Analysis of different sources reveals that in the United States and Canada recycled concrete aggregate is used as an inert substitute for stabilised bases (100% utilisation in 6 USA states and in 2 Canadian, in lower amounts in others) or granular bases, stabilised or granular sub-bases (4+2 at 100%) and subgrades (3+1 at 100%), as well as in hot mixes for shoulders (5+2 at 100%). In some regions (Arizona, Oregon, Missouri, Long Island) all the demolition material is reused in road pavements, covering a significant quota of the annual requirement for inert material [4-6].

In Austria, the aggregate obtained from recycled concrete has been used, after stabilisation with cement, in the realisation of the protective capping layer of motorway pavements [7]; it has also been used for the grading adjustment of granular sub-bases when re-facing superstructures subject to heavy traffic [8].

In Germany, recycled demolition debris (also of pavements) have been used in urban and rural roads to construct load-bearing bases stabilised with cement [9], but the reuse of recycled material has not even been scorned in the construction of unbound motorway bases [10-12].

Analogous experiments to the German ones are reported in Belgium, aimed at the reuse of waste materials as base materials [13] or in embankments, sub-bases and crushed stone bases [14].

In Holland C&D wastes have been used mainly for hydraulic bounded sub-bases of rural roads [15].

In the Czech Republic, recycled cement aggregate has been used extensively in the re-surfacing of Runway 06/24 at Prague Airport [16], both for the grading correction of the stabilised sub-base and the integral substitution of natural material 0/45 in a 20 cm hydraulic binder base course.

In Italy, as well as the more traditional use of marginal materials in Reclaimed Asphalt Pavements (RAP), the use of C&D debris is cited in cement bound granular materials for base courses [17] in the Marche Region.

In the UK, even although the conformity of concrete recycled to the "Type 1" specification has been ascertained, given the lack of any standards on the use in the construction sector [18], limited interest has been shown in the re-use of this material in road works.

3. THE RECYCLING OF DEMOLITION DEBRIS IN ITALY. EXISTING AND PROSPECTIVE REGULATIONS

3.1. The Regulations

In Italy, the law regulating the disposal, treatment and reuse of this type of waste is the Legislative Decree 5.02.97 no. 22, named the "Ronchi Decree" [19], issued to put into effect the European Union Directive no. 91/156/EEC on wastes, no. 91/689/EEC on dangerous wastes and no. 94/62/EEC on packaging and packaging wastes. This legislative measure, that succeeded in putting a sector that had been subject to changeable and confusing regulations in order, constitutes a point of strength in the current policy of environmental protection as it disciplines a subject that in virtue of its many implications, strongly influences the most disparate human activities.

A first merit of the L.D. no. 22/97 is classifying wastes in relation to their "life cycle" and not exclusively by their nature, thus including all the processes that go into their production, treatment, disposal and eventual reuse in the evaluation of their danger.

Another positive aspect (as would be expected) of the legislation is the sufficiently precise identification of the competence of those involved in the cycling of wastes (companies, local authorities, private individuals) and the definition of the related duties, limitations and responsibilities.

On the other side, on the strength of past experience, the Decree places fairly severe constraints on the activities of recovery or reuse of the wastes, providing for heavy sanctions in all cases, even slight, of non-fulfilment. This might be acceptable for some types of wastes with a high risk potential (industrial, hospital, human wastes...), but not for others that, by their very nature, are inert substances, only occasionally contaminated by pollutants that are easily identified and separated (for example, C&D wastes).

It follows that, in Italy, the reuse of discarded building materials today appears to be a generally complicated and onerous business for two main reasons: the complexity of the bureaucratic procedures for authorisation, subject to stringent regulatory constraints (with relevant risks in the case of even accidental non-fulfilment); the need to use advanced technologies and treatment procedures of the material to safeguard against the sanctions provided for those who handle toxic wastes improperly.

It can, however, be said that, despite the regulatory framework described, not all operators involved in the reuse of C&D wastes have been discouraged by the Law. In the Veneto Region, where Padua University is situated, there are many firms, some fairly big, involved in recycling discarded building materials (buying the debris, treatment, sale, occasionally using the substitute inert material), also in parallel to the traditional activity of excavation.

3.2. Treatment methods for demolition waste

According to the Law in force, the treatment of demolition waste is in two successive stages: the collection of the debris and their treatment in the recycling plant.

The composition of the final product of the treatment is defined at the collection stage and is strictly dependent on the building type being demolished. Generally, the composition changes with the geographical areas: in the USA and Denmark the debris are 80% concrete, 10% wood, with the rest miscellaneous (bricks are scarce as they are not included in the construction standards of these countries). In Germany almost 90% of the material from demolition is brick or concrete (in about equal quantities), but there is also a significant quota of plastic materials (4%).

In Italy, the material from demolition is on average 80% bricks and concrete; 10% waste from digging activities; 5% demolished pavements; 3% metals; the last 2% being different materials (plastic, wood, cellulose wastes, ceramics...). The composition varies with the origin of the debris: as is natural, industrial buildings provide mainly concrete, residential buildings concrete and bricks, road pavements inert materials and bituminous binders.

The nature of the aggregate extracted following treatment of the debris varies according to the source of the raw materials: the bricks supply mainly flattened inert material, the concrete guarantees more polyhedral particles.

In general, the catch basin of C&D debris is homogeneous and defined for each firm, so that, even with the heterogeneity of the demolished structures, there is a certain constancy in the composition characteristics of the treated material. In any case, there are storage areas for the differentiation of the wastes and a pre-selection of the components to pass to the crushing plant, guaranteeing the uniform production over time, that is imposed by all the road and airport specifications.

Treatment of the materials is done in mobile plants, spread over the territory close to the debris deposits or big yards, or in centralised plants with higher capacity and production quality. In these plants pre-selection, elimination of pollutants, crushing and screening of the material is carried out. The plants must have a low environmental impact, so by law they must be equipped with dust abatement systems and be suitably soundproofed.

In Italy, C&D wastes are treated in fixed plants mainly according to the R.O.S.E (Recupero Omogeneizzato Scarti Edilizi = homogenised recovery of building debris) technology, which provides the following functioning plan (Figure 1).

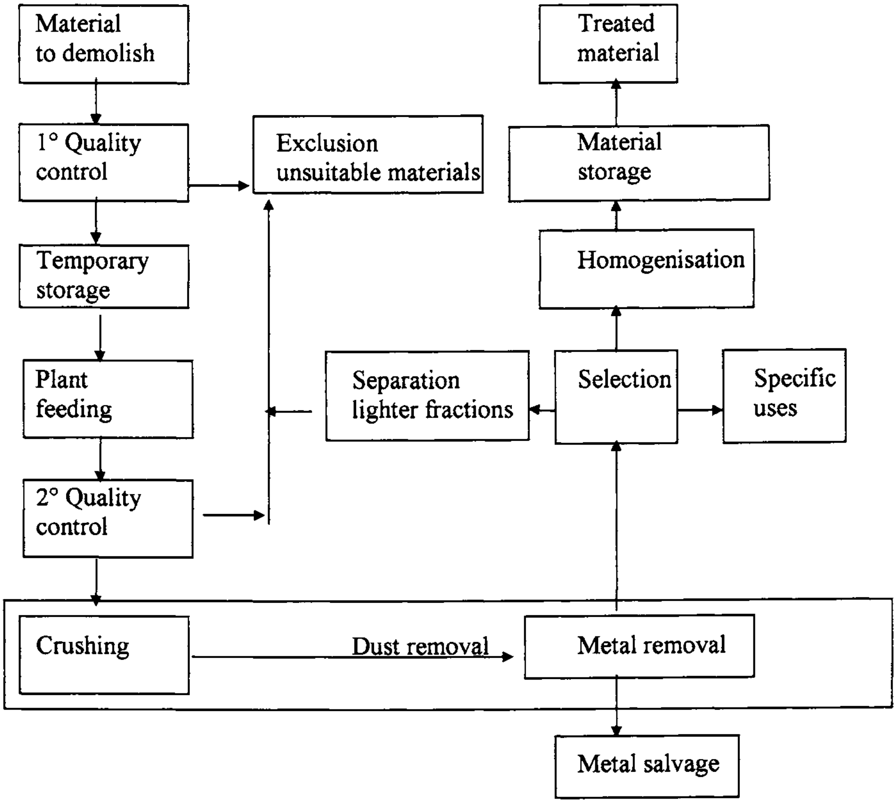

Figure 1. R.O.S.E. Technology.

The critical stage of this method is the feeding of the plant, done by a vibrating barred device, fed by the loading hopper, to eliminate the 0/80 mm loose fraction, made up of earth, plaster flakes, bricks and wood, for which crushing is useless. Sieving eliminates the 0/10 mm size, the remaining fraction then being positioned above the crushing device. The material goes down a slide into the crushing chamber, rotates around the mill rotor and comes out at the bottom, where it is collected by a shaking channel (wide enough to avoid obstructions) and a conveyor belt (isolated against dust dispersal, then settled by water vaporisers or filtered suction devices).

The crushed material is conveyed to a sieve that selects two different sizes of material (if necessary working in closed circuit with the crushing chamber or in series with a conveyor belt that carries the inert material for further screening for specific uses). The lighter fractions are eliminated from the rest of the treatment by ventilating and suction devices, while the resulting material, after homogenisation, is sent for storage.

Crushing is done with jaw presses, rotating or hammer crushers. The former can be made up of a primary crusher to break up coarser material (in large blocks) and a secondary crusher to work the already treated material, so guaranteeing a greater variety of sizes. The rotating crushers, that are often used as devices for secondary crushing in the mining industry, are particularly suitable if built with tanks with moveable sides for use as single-stage crushers (secondary crushing is unnecessary because of the relative friability of the demolition debris). In comparison to the jaw crushers, they allow a wider range of materials to be treated (including wood and bituminous conglomerates that crumble or stick in the jaws, making separation difficult).

4. C&D DEBRIS USED IN THE EXPERIMENTS

The material used in the experiments derives from a crushing treatment of demolition debris by a rotating mill. The crusher is a 1995 German-built HAZEMAG AP (at first rotation) PH (sides operated by a hydraulic system with centralised control), with a reinforced rotor with 4 hammers (diameter 1340 mm and nominal width 1300 mm). The rotating mill (the moving parts of which are in high-grade manganese steel) weighs 17,500 kg; the feeding capacity is in the order of 200 t/h for a product of 0/71 mm size but can be increased to 250 t/h for 0/150 mm size.

The presence of moveable sides is of particular advantage in the treatment because it renders the rotor action independent from the weight of the machine and allows the capacity of the crusher to be adapted to the sizes of the blocks being treated or blocks less capable of being deformed (e.g. steel beams). "Selective" crushing guarantees an immediate and safe separation of the reinforcement from the concrete. The size of the rotor allows the treatment of whole blocks of reinforced concrete (railway sleepers, ceiling rafters, fencing posts...), reducing to the final dimensions with a single pass. The only disadvantage of the system is the considerable wear and tear to the mechanical parts, which can be overcome by using standardised modular components that are readily available and easily maintained.

The plant used for the production of the discarded building materials used in the research did not include a homogenisation phase, as the inert material already presented the geometrical and physical characteristics necessary for use. Storage was in piles.

The inert materials had particle sizes 0/71 and 0/40 mm, suitable for use in road and airport embankments, sub-bases and foundations. The chemical and mechanical tests necessary to verify the suitability for use in the building sector were carried out on these fractions.

A study of the composition revealed the following differences between the tested

Table 1.
Composition of the marginal material

Composition of the treated material	*Particle size 0/71 [%]*	*Particle size 0/40 [%]*
Mortar and fine inert material	25	30
Bricks	45	40
Coarse inert materials, also covered with mortar	30	30

materials (Table 1).

The inert material underwent the characterisation trials traditionally used for natural aggregates, the results of which were compared with the standards of the specifications in force in the roads and airports sector. Previously, it was wished to verify the efficiency of the crushing treatment, determining the shape and flattening index of the material (in the senses of the CNR standard 95/84 [20]), also as quality controls of the inert material (Table 2).

Table 2.
Shape of the aggregate

Test	*Unit measure*	*Particle size 0/71*	*Particle size 0/40*
Shape Index	%	18	10
Flattening Index	%	16	12

The chemical compatibility of the discarded building materials was ascertained using the leaching test with acetic acid 0.5 M, following the procedure standardised in Italy by CNR-IRSA. The results are compared below against the limits provided for in the regulations currently in force (tab. A of Law no. 319 of 1976 [21]), demonstrating complete suitability of the material that, according to the current standards, can be considered "inert waste" (Table 3).

The physical-mechanical properties of the two particle-sizes of recycled aggregate were ascertained separately for the single fractions, using the Italian standard of the Consiglio Nazionale delle Ricerche (CNR – National Research Council) as reference.

Table 3.
Chemical characterisation of C&D debris

Parameters	*Pb*	*Cd*	*Cu*	Cr^{VI}	*Fe*	*Mn*	*Ni*	*Zn*	pH_{start}	pH_{end}
Legal limits [mg/l]	0.2	0.02	0.1	0.2	2	2	2	0.5	-	-
Ceding [mg/l]	< 0.01	0.02	< 0.01	0.04	0.16	0.45	0.06	0.22	11.00	5.00

5. THE REUSE OF DISCARDED BUILDING MATERIALS IN EMBANKMENTS AND SUBGRADES

The Italian standards that discipline the construction of road embankments appear in Official Bulletin no. 10006, issued by CNR-UNI in 1963 [22]. These standards fix some precepts of a general nature for an aggregate for the construction of road embankments; it must be clean, i.e. free from twigs, roots and organic materials, well compacted, with a density level above 90% of the AASHTO standard or modified density; not sensitive to frost. It must also conform to a soil of the type A1, A2, A3 or A4 in the Italian classification that is drawn entirely from the H.R.B. classification in the AASHTO M 145-49 standard.

The soils with which the subgrade is made up should belong preferably to classes A1, A2 and A3; the on-site density must be higher than 95% of the AASHTO standard or modified density; the deformation modulus, determined by load-bearing trials on a slab (currently in the sense of CNR B.U. no. 146/92 [23]), must be no lower than 150 daN/cm^2.

Current specifications provide few further, but more constraining requisites for acceptance of the aggregates: the material of the subgrade can belong to class A2, limited to sub-classes A2-4 and A2-5, thus resulting as preferable to a soil A3; the deformation modulus of the subgrade must be greater than 500 daN/cm^2.

As the discarded building materials were to be used in the construction of road embankments, the 2 particle sizes produced were then classified (Table 4).

The laboratory trials confirm the suitability of the recycled material for use in embankments and subgrades. Another requisite for the evaluation of the substitute material, the compactibility of the inert material, was then ascertained by means of the traditional Proctor trial (AASHTO) modified (in the senses of CNR B.U. no. 69/78 [24]), that provides a relative indication of its behaviour under different trial conditions (on site and in the laboratory).

6. REUSE OF DISCARDED BUILDING MATERIALS IN ROAD BASES AND SUB-BASES

6.1. Experimental set-up

The construction of sub-bases and road bases is disciplined by the more recent CNR B.U.

Table 4.
CNR-UNI (AASHTO/HRB) classification of 0/71 and 0/40 marginal aggregate

Property	*Particle size 0/71*	*Particle size 0/40*
Passing sieve n. 10 ASTM [%]	18.3	25.8
Passing sieve n. 40 ASTM [%]	10.2	15.1
Passing sieve n. 200 ASTM [%]	4.3	7.4
Plasticity Index [-]	Non-plastic	Non-plastic
Group Index [-]	0	0
CNR-UNI 10006/63 TYPE	*A1-a*	*A1-a*

no. 139/92 standard [25], as well as by the previously cited CNR-UNI 10006/63 standard.

Both set the conditions of use of granular materials in road foundations and bases; also for these materials forming part of mixtures with hydraulic binders, corresponding to two separate types: "stabilisations" with cement and "cement bound granular mixes" (the latter also regulated by CNR B.U. no. 29/72 [26]). Given that the road and airport specifications also set conditions of use for aggregates in the sub-bases of pavements, the existence of a fairly variegated regulatory framework can be deduced. The following Tables 5-7 compare the properties of the tested materials with those provided for in some of the standards and specifications currently in force (ANAS, Azienda Nazionale Autonoma delle Strade – National Road Board [27]).

Table 5.
Comparison between particle-size curves of the recycled material and grading envelope in the standard

Sieves [mm]	*ANAS Sb [%]*	*CNR-UNI sb I/A [%]*	*CNR-UNI sb I/B [%]*	*ANAS cbm sb/b [%]*	*CNR 29/72 sb/b A1[%]*	*CNR 29/72 sb/b A2[%]*	*0/71 Grading*	*0/40 Grading*
71	100	100	-	-	-	-	100	-
40	75-100	-	-	100	100	100	84.6	100
30	-	70-100	100	80-100	-	-	80.6	100
25	60-87	-	-	72-90	65-100	65-100	75.7	86.8
15	-	-	70-100	53-70	45-70	45-78	52	67.3
10	35-67	30-70	50-85	40-55	35-60	35-68	40.2	52.1
5	25-55	23-55	35-65	28-40	23-45	23-53	31.2	36.7
2	15-40	15-40	25-50	18-30	14-30	14-40	18.3	25.8
0.4	7-22	8-25	15-30	8-18	6-14	6-23	8.1	10.2
0.075	2-10	2-15	5-15	5-10	2-7	2-15	4.3	7.4

Table 6.
Comparison between properties of the recycled material and standards for not bound mixtures

Property	*ANAS sb*	*CNR-UNI sb I/A*	*CNR-UNI sb I/B*	*CNR 139/92 sb*	*0/71 Grading*	*0/40 Grading*
E.S. [%]	25-65	-	-	> 40	41	42
L.A. [%]	< 30	-	-	< 30	39	34
C.B.R. [%]	> 50	> 50-80	> 50-80	-	81	-
G [%]	-	*	*	< 30	15	12
PI [%]	-	< 6	< 6	NP	NP	NP

Table 7.
Comparison between properties of the recycled material and standards for mixtures bound with cement

Property	*CNR-UNI sb I/A*	*CNR-UNI sb I/B*	*ANAS cbm sb/b*	*CNR 29/72 sb/b A1*	*CNR 29/72 sb/b A2*	*CNR cbm 139/92*	*0/71 Grading*	*0/40 Grading*
E.S. [%]	-	-	30-60	> 35	> 25	> 35	41	42
L.A. [%]	-	-	< 30	< 30	< 30	< 30	39	34
C.B.R. [%]	> 50-80	> 50-80	-	-	-	-	81	-
G [%]	*	*	-	*	*	< 30	15	12
PI [%]	< 18	< 18	NP	NP	< 6	NP	NP	NP
$C_{s,7}$ [N/mm^2]	2-7	2-7	2.5-4.5	3-7	3-7	-	-	1.8-3.9
$T_{s,7}$ [N/mm^2]	-	-	> 0.25	-	-	-	-	0.27-0.3

Legend:
ANAS sb: ANAS granular sub-base
CNR-UNI sb I/A: CNR-UNI 10006 (granular/cement stabilised) sub-base Type I/A [22]
CNR-UNI sb I/B: CNR-UNI 10006 (granular/cement stabilised) sub-base, Type I/B [22]
ANAS cbm sb/b: ANAS (sub-base or road base) cement bound granular material [27]
CNR 29/72 sb/b A1: CNR B.U. n. 29/72 (sub-base or road base) cement bound granular material, Type A1 [26]
CNR 29/72 sb/b A2: CNR B.U. n. 29/72 (sub-base or road base) cement bound granular material, Type A2 [26]
CNR 139/92 sb: CNR B.U. n. 139/92 granular sub-base [25]
CNR 139/92 cbm: CNR B.U. n. 139/92 (sub-base or road base) cement bound granular material [25]
0/71 Grading: Aggregate of 0/71 mm particle size from treatment of C&D wastes
0/40 Grading: Aggregate of 0/40 mm particle size from treatment of C&D wastes
E.S.: Equivalent in Sand (according to the CNR B.U. standard n. 27/72 [28])
L.A.: Los Angeles coefficient (according to the CNR B.U. n. 34/73 [29])
C.B.R.: C.B.R. Index (according to the CNR-UNI standard 10009/64 [30])
G: Frost susceptibility (according to the CNR B.U. standard n. 80/80 [31])
PI: Plasticity Index (according to the CNR-UNI standard 10014/64 [32])
$C_{s,7}$: Compressive strength, after 7 days
$T_{s,7}$: Tensile strength, after 7 days
-: Limit value not defined
*: Parameter determined by alternative procedures
NP: Non-plastic

The experimental trial was split as follows:

1. 0/71 aggregate, not bound: particle-size analysis; Atterberg limits; equivalent in sand; Los Angeles test; susceptibility to frost; C.B.R. carrying capacity; compaction according to the modified Proctor procedure, with definition of density and optimal moisture content.
2. 0/71 aggregate, in cement stabilisation (binding agent content between 3 and 5%): optimisation through C.B.R. carrying capacity trials after 7 days of ageing and 4 days soaking in water.
3. 0/40 aggregate, not bound: particle-size analysis; Atterberg limits; equivalent in sand; Los Angeles test; susceptibility to frost; compaction according to the modified Proctor procedure, with definition of density and optimal moisture content.
4. 0/40 aggregate, in cement-bound granular material (binding agent content between 3 and 5%): optimisation through compressive strength tests after 7 days of ageing; indirect tensile test; determination of the secant elastic modulus; determination of the dynamic elastic modulus.

Routine trials conducted on the recycled aggregate demonstrated the similarity to natural aggregate. The only result not conforming to the standards was the value of the Los Angeles coefficient (see Tables 6, 7), obviously worse for the larger particle sizes as this denoted the greater amount of bricks in the coarser fractions of the inert material. In the light of the data obtained in the trials, however, it must be admitted that resistance to crushing is not the most representative index of behaviour, given that the mechanical analyses were otherwise positive.

6.2. Particle-size 0/71 characterisation

The compaction test on the aggregate 0/71 indicated the maximum reachable density to be 1.86 g/cm^3 in the laboratory, with an 8% moisture content (Figure 2); the density of the material, measured with a shaking table (CNR B.U. no. 76/80 [33]) was 1.36 g/cm^3.

The material is generally sensitive to moisture, especially with moisture contents lower than the optimal one; in reality, variations in moisture content of 2 % are needed to produce reductions in density below 98 % of the maximum value. Particular attention is therefore

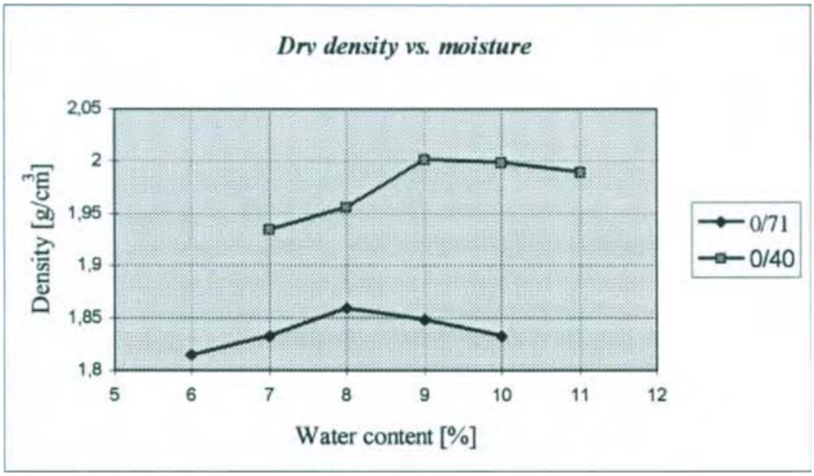

Figure 2. Modified Proctor (AASHTO) compaction test.

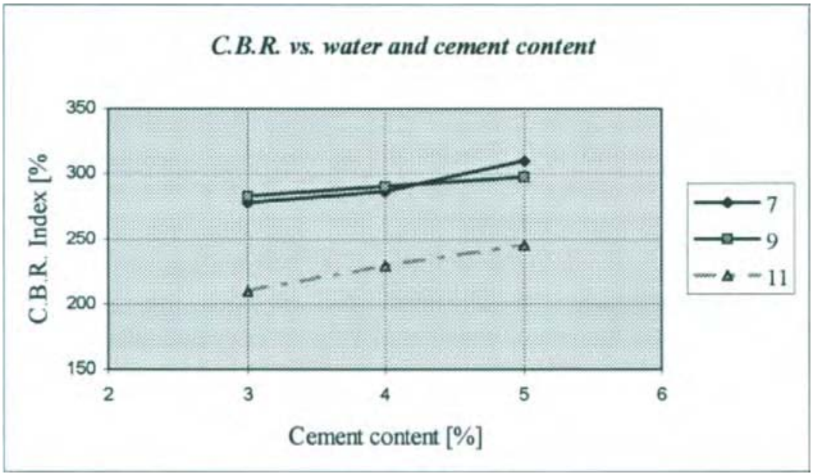

Figure 3. C.B.R. test on 0/71 aggregate stabilised with cement.

required when using the aggregate, especially in the saturation and compaction phase.

After stabilising the 0/71 mm particle-sized recycled aggregate with cement (binding agent dose 3-5%; moisture content 7-9%, close to the optimal value), the carrying capacity was tested using the C.B.R. test on samples aged for 7 days in a thermostatic cell at 20° C and 90% humidity. The samples were soaked for a further 4 days before the penetration trials. The C.B.R. values previously measured on the not bound material, clearly increased, in some case even quadrupling; no swelling of the samples was registered (Figure 3).

The bearing capacity increase resulted as being proportional to the dosage of binding agent, even although this effect was shown to be more appreciable at higher moisture contents. The optimal amount of water also moved towards lower values than those obtained with the not bound aggregate. Also in this case it must be pointed out that the amount of water is crucial, as it has repercussions on the compactibility and resistance of the material when used.

6.3. Particle-size 0/40 characterisation

The compaction test on the 0/40 aggregate indicated the maximum reachable density to be 2.01 g/cm^3 in the laboratory, with a water content just above 9% (see Figure 2; the increase being explained by the greater specific surface area of the inert material); the density of the material, measured with a shaking table (CNR B.U. no. 76/80 [33]), was 1.44 g/cm^3.

The material is generally sensitive to moisture for water contents lower than the optimal one; variations in moisture content of 2% reduce the density to 96% of the maximum value; *vice versa*, the sensitivity to excessive wetting appears to be low. As already shown in other studies [1], the absorbent effect represents a characteristic element of the discarded building materials.

The 0/40 mm particle-size aggregate was then used to make up mixtures known as "cement bound granular materials" that, compared to the cement stabilisations, are higher quality conglomerates with better physical-mechanical characteristics, despite dosages of binder even lower (from 2.5 to 3.5% according to ANAS [27], from 3 to 5% according to the CNR standards [26]; 4-12% is given by the CNR-UNI 10006 standard for the stabilised ones [22]).

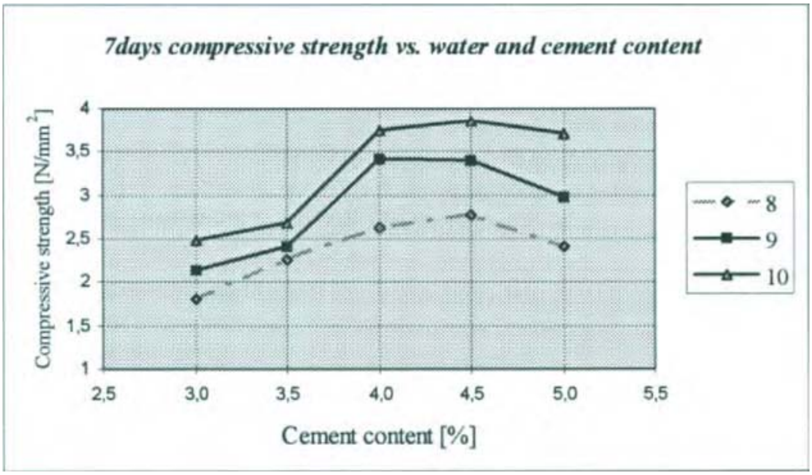

Figure 4. Compressive strength of "cement bound granular materials".

A cement content of between 3 and 5% was used for the 0/40 aggregate, varying the moisture content around its optimal value. The mixture was optimised using the simple compression test on cylindrical samples (C.B.R. sample sizes) aged for 7 days at 20° C and 90% humidity. The optimal dose of cement was found to be 4.5% for each moisture content; in these mixtures the resistance to compression varied between 2.8 and 3.8 N/mm^2, always higher than those given in the Specifications [e.g. 27] (Figure 4).

Further mechanical trials were done on the mixture made up with 10% water and 4.5% cement:

- resistance to compression was determined after 14 and 28 days of ageing at 20° C, 90% humidity, on samples made in C.B.R. moulds; resistance in the order of 4.8 N/mm^2 was reached, with increases of 22% in 3 weeks (Figure 5);

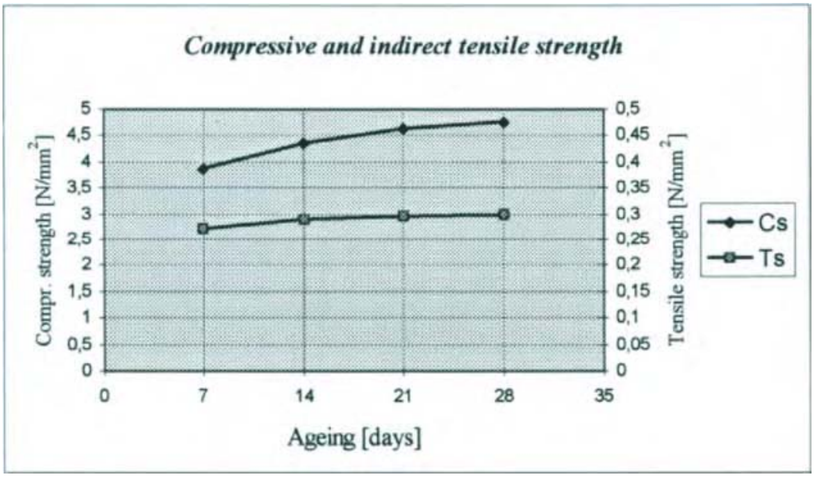

Figure 5. Mechanical properties of "cement bound granular materials".

- the indirect tensile strength was determined after 7, 14 and 28 days of ageing on samples made in C.B.R. moulds, according to the indications in the CNR B.U. standard no. 97/84 [34]; the resistance at 7 days was compatible with the requirements in the standard (0.27 N/mm^2), but varied little over time (increasing by 11% in the following 3 weeks) (Figure 5);
- the secant elastic modulus was determined according to the UNI 6556 standard (commonly adopted for concrete [35]), on prismatic (15x15x45 cm) and cylindrical C.B.R. samples; the cylindrical and prismatic samples always gave similar values (8% difference after 7 days, 2% after 28 days); after 28 days the elastic modulus was higher than 5,000 N/mm^2 (Figure 6);
- the dynamic modulus was determined according to the UNI 9524 standard [36] by means of ultrasonic tests, on prismatic (15x15x45 cm) and cylindrical C.B.R. samples; in this case the cylindrical samples always gave slightly higher values than those of the prismatic samples (2% difference), varying between 8,200 and 9,300 N/mm^2 between 7 and 28 days ageing (Figure 6).

The results obtained from the mechanical tests on cement bound granular materials, consisting of C&D wastes, are undoubtedly positive. Their examination calls attention to the fact that the dosages of cement used (much lower than those of concrete, even lean) act mainly on the elastic properties of the material (shown by the compressive strength and by the modulus) rather than on the cohesion of the mixture (shown by the tensile strength).

The static modulus and the dynamic modulus differ substantially, not just because they represent different modes of behaviour of the material, but also, probably, because of the different testing procedure used in their determination. Their laws of variation also differ.

In the long-term, the relationship between the static and dynamic modulus is not unlike that found in concrete, so it is considered that the classic time limit of 28 days for characterising mechanical behaviour can also be used for the cement-bound granular material.

Lastly, it can be admitted that the shape of the sample tested in the laboratory does not appear to be relevant if it is true that the variations in the measured parameters on the

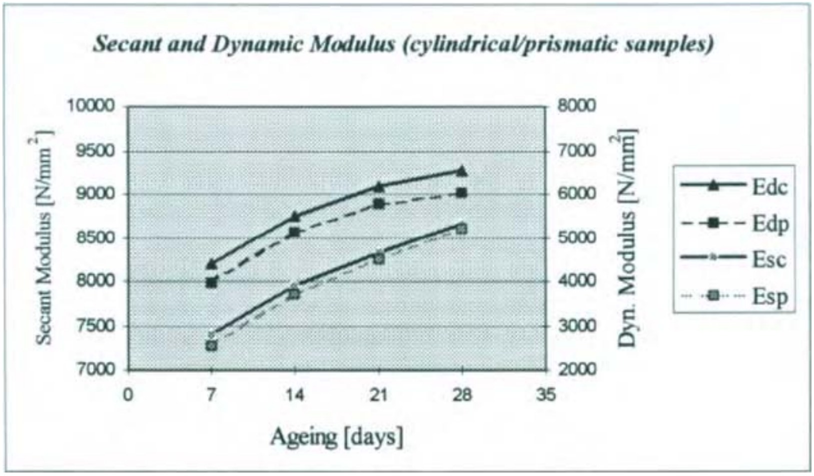

Figure 6. Secant and dynamic modulus of "cement bound granular materials".

cylindrical and prismatic samples come within the tolerance of the single measure. The cylindrical samples certainly overestimate the resistance of the material.

7. CONCLUSIONS

Research was conducted to verify the possibility of using discarded building materials in constructing embankments, subgrades, sub-bases and road bases. Two different particle sizes of aggregate (0/71 and 0/40 mm) were used after treatment of demolition debris from civil engineering structures in a rotating mill.

Chemical characterisation demonstrated that the material is inert and does not determine dangerous interactions with the environment under normal working conditions.

The physical-mechanical characterisation allowed substantial equalising of the recycled aggregate to natural stone aggregate. Only one parameter, the Los Angeles coefficient, was higher than that allowed in the standards, but this aspect should not be overrated as other elements show that: the polyhedral shape of the granules, especially in the smaller particle-size fraction; the fact that foreign standards and specifications set lower acceptance limits than the Italian ones; the positioning of the materials within the superstructure or infrastructure, that as a rule, makes the properties monitored in this trial not very significant.

The tests on mixtures of recycled aggregate and hydraulic binder (cement stabilisations,, cement bound granular materials) demonstrated that the properties of the residual materials can be enhanced if required, for more exacting uses than those in embankments and sub-bases.

Besides the above considerations, it also emerged from the research that:

- the properties of the material depend on its homogeneity, ruled in turn, by that of the debris that it is derived from;
- there must be a strict relationship between mix-design in the laboratory and application of the material on site, as it has been demonstrated that the characteristics of the mixtures containing the substitute are particularly correlated to the dosages of the components;
- in the short-term, the mixtures with the hydraulic binder are more than appropriate for use in superstructures, but in the medium-term some properties improve significantly (static elastic modulus).

Considering that the annual production of natural aggregate excavated in Italy is around 250 million tonnes, against a requirement of more than double that in the building sector, the importance can be understood of procuring alternative resources to the natural materials. The availability of C&D wastes could resolve this problem, as it is estimated that the amount of debris produced could cover, within a few years, the aggregate requirements in excess of the natural resources, that are in any case destined to reduce over time.

The economies of recycling are beyond dispute; even leaving out the economies coming from lower environmental impact and saving of natural resources, it can be noted that:

- the cost of disposal in controlled dumps (up to 7 US$/tonne) would be cancelled out;
- the demolition company could even sell the residual material to the processing company, giving profit margins to the latter;
- the recycled and treated material could be sold at between 80-90% of the cost of natural material, meaning earnings for the producer and savings for the buyer;
- the sale of metals extracted from the debris could cover a relevant part of the running costs of the treatment plant.

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Variation in mechanical properties of MSW incinerator bottom ash
Results from triaxial tests

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ABSTRACT

This study deals with laboratory testing of municipal solid waste (MSW) incinerator bottom ash. The aim was to investigate the mechanical properties such as stiffness and stability of the ash for future use in unbound road layers. Especially the effect of the material variation on the mechanical properties was analysed. Specimens of bottom ash from four different plants and four seasons were tested by repeated load triaxial tests. Results so far suggest that there is a significant variation in the mechanical properties, both seasonal fluctuations and differences between incinerator plants. However, the variation is not greater than for studied natural aggregates. It is also shown that the organic content has a limiting effect on the resilient modulus, as expected. If MSWI bottom ash is utilised instead of sand in a capping layer, the same design modulus could be used as for the sand. All tested materials are stable and give reasonable permanent deformations at the stress level that is relevant for a Swedish capping layer.

1. INTRODUCTION

Despite Sweden's relative richness in natural aggregate reserves, there is a governmental ambition to facilitate and increase the use of alternative materials in Swedish road constructions. Several research projects are going on in purpose to establish both design and environmental guidelines. One material that has not been used in Sweden in large-scale projects yet, is bottom ash from incineration of municipal solid waste, here called MSWI bottom ash.

This study deals with laboratory testing of unbound MSWI bottom ash. The aim was to investigate the mechanical properties of the ash when used in unbound road layers, at first hand in capping layers. Great variations in the ash properties were expected, due to seasonal variations in the waste. Different incineration processes could also be expected to have an influence on the mechanical properties of the bottom ash. Therefore, ashes from different seasons and different incineration plants were studied.

MSWI bottom ash from four plants was chosen, namely from Stockholm, Gothenburg, Malmö and Linköping. These plants incinerate both municipal and industrial wastes. They are among the largest in Sweden and produce both heat and electricity.

The production of bottom ash for each of the stations is between 35 000 and 80 000 metric tons per year, as can be seen in table 1. This can be compared to the total amount for Sweden, which was about 340 000 metric tons in 1997.

Table 1. Production statistics for incineration stations (1)

Station	Incinerated waste (1 000 kg)	Energy production (MWh)		Remainder (1 000 kg)	
		Heat	Electricity	Bottom ash	Fly ash
Högdalen, (Stockholm)	263 896	588 473	22 397	51 912	13 263
Gothenburg	381 500	1 038 040	129 418	79 302	13 457
Malmö	202 166	573 749	No prod. 1997	36 850	4 410
Linköping	225 585	655 691	117 852	49 500	9 501

2. METHODS

The Swedish Geotechnical Institute (SGI) made sampling in the plants as part of another study. The sampling was carried out during different times of the year, approximately every third month. Then, the 16 materials were stored outdoors for at least six months in wooden boxes without roofs. From these boxes representative samples were taken for this study.

The mechanical properties were studied using repeated load triaxial tests. Complementary properties such as composition, particle size distribution, organic content, optimum water content and maximum dry density were also investigated. Comparison with corresponding properties of conventional materials, such as different sandy materials was made. SGI has done chemical and environmental characterisation on the same material and those results will be reported separately.

In the repeated load triaxial tests, the material deformation under simulated traffic conditions is investigated. The resilient strain is used to calculate the stiffness expressed as resilient modulus and the accumulated permanent deformation can be used for classification purpose. Since the specimen exposed to loading consists of the whole composite material up to a certain grain size, it is in fact the function of the material that is tested. The method is well known both for fine-grained and coarse-grained materials and a CEN standard is under development.

The tests were carried out on undrained specimens with the dimensions of 150 mm diameter and 300 mm height in VTI:s servo-hydraulic material testing system (VMS). This allowed ashes with maximum particle size up to 30 mm to be tested. The specimens were undrained since this is most similar to reality. The traffic load is quick compared to the long time loading that is used in soil mechanics. The specimens were manufactured in *one* layer by means of vibrating compacting equipment called Vibrocompresseur in a special cylinder. This is a "friendly" method that was chosen because earlier experiments showed crushing tendency for these materials. After compaction the specimens were pushed out of the cylinder and equipped with platens in both ends and a thin rubber membrane around.

The aim was to test all materials at the same relative water content and the same relative density. The conditions that were chosen were optimum water content and 90 % of maximum dry density from modified proctor. However, problems in compacting some of the specimens resulted in differences in the attained compaction degree. The impact this fact has had on the test results is discussed later.

For each material investigated, three specimens were compacted and tested. The results that are discussed here are averages for these three specimens. The tests are still carried on and will be finished during this year.

3. RESULTS

The stations produce bottom ash with grain size distributions according to figure 1.

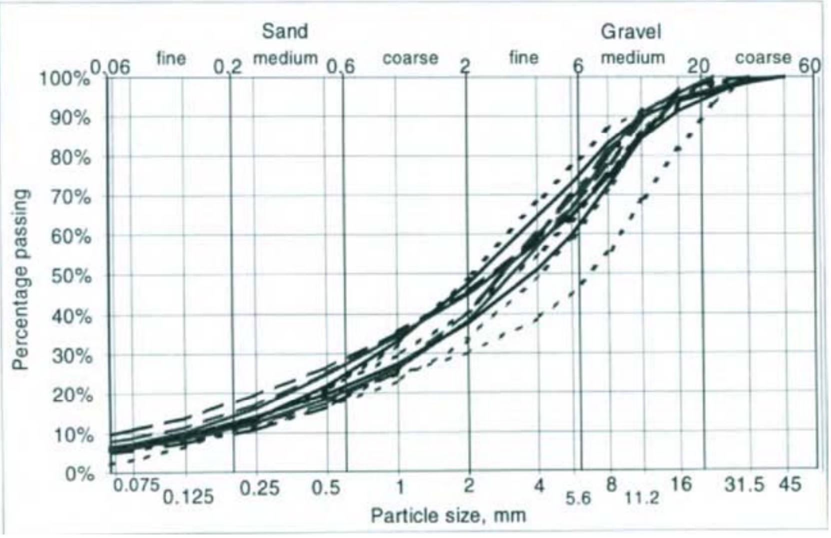


Figure 1. Grain size distribution for MSWI bottom ash from four different stations and three different seasons.

SGI has carried out compaction tests on the materials by means of modified proctor. The same institute has also reported organic content measured as loss on ignition (LOI) for the studied materials. Table 2 and 3 summarises the results so far.

Table 2. Maximum dry density and optimum water content, from modified Proctor tests (from SGI).

	Stockholm		Gothenburg		Malmö		Linköping	
Season	Max dens (t/m^3)	Opt w (%)	Max dens (t/m^3)	Opt w (%)	Max dens (t/m^3)	Opt w (%)	Max dens (t/m^3)	Opt w (%)
Autumn	1,61	13,5	1,73	17	1,65	15-18	1,58	18,0
Winter	1,66	9,0	1,72	16,1	1,63	16,5	1,48	19,5
Spring	1,58	11-19	1,66	17-19	1,64	16,4	1,43	20,5

Table 3. Loss on ignition (LOI) in %, sample A/sample B. (from SGI)

	Stockholm	Gothenburg	Malmö	Linköping
Autumn	3,9/4,1	2,8/4,0	3,8/3,8	6,5/7,0
Winter	3,2/4,0	2,7/2,7	4,4/4,4	9,1/9,2
Spring	4,1/4,3	3,7/3,7	4,9/5,0	8,9/9,0

Furthermore, SGI has investigated the environmental properties by leaching tests on the same materials. Results from these investigations will be reported separately by Dr Ann-Marie Fällman.

3.1. Stiffness and stability

Data from triaxial tests on bottom ash from four stations and three seasons are presented here. In figure 2 the stiffness expressed as resilient modulus for different stresses is plotted for one of the stations. Results from the other stations showed the same pattern.

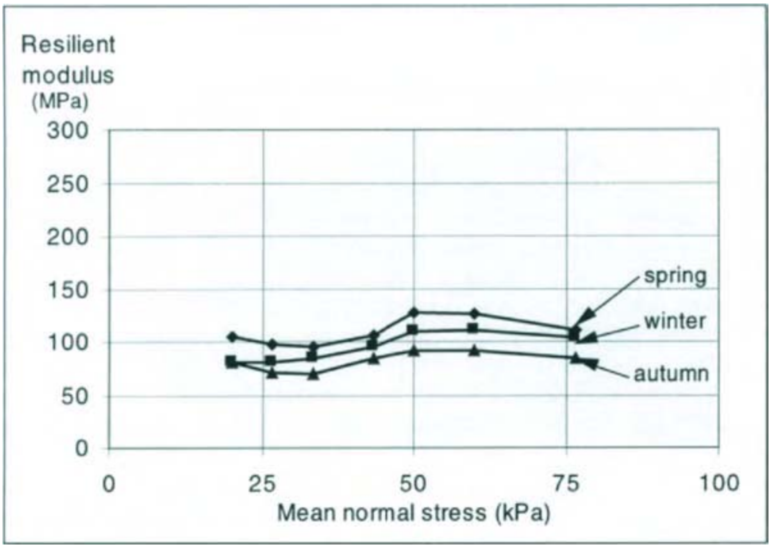


Figure 2. Stiffness expressed as resilient modulus for MSWI bottom ash from Stockholm.

Two things can be noticed. First, the curves are rather flat, which indicates a weak stress dependency and is typical for sandy materials. Second, the differences between "spring", "winter" and "autumn" ashes are significant.

However, the relative position of curves, with the "spring" modulus being higher than "winter" and "autumn" modulus, is not general. This is illustrated in figure 3, where the results from one stress condition are compared for all four stations. The scatter among the three specimens tested for each material is also illustrated. Some of this scatter and also the variation between materials can be explained by unintended differences in density of the specimens. This is discussed in a subsequent chapter.

The stability expressed as permanent compressive deformation will also be evaluated within this project. Preliminary results suggest that the permanent deformations are very small as long as the mean normal stress is less than 60 kPa. In figure 4 the deformations at a mean normal stress of 50 kPa are compared.

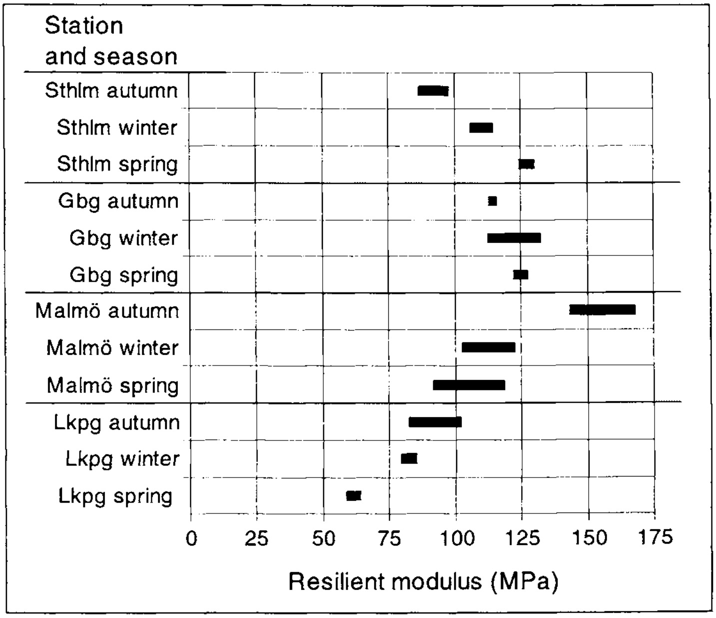


Figure 3. Variation in resilient modulus at one stress condition.
5 % significance. Mean normal stress = 50 kPa.

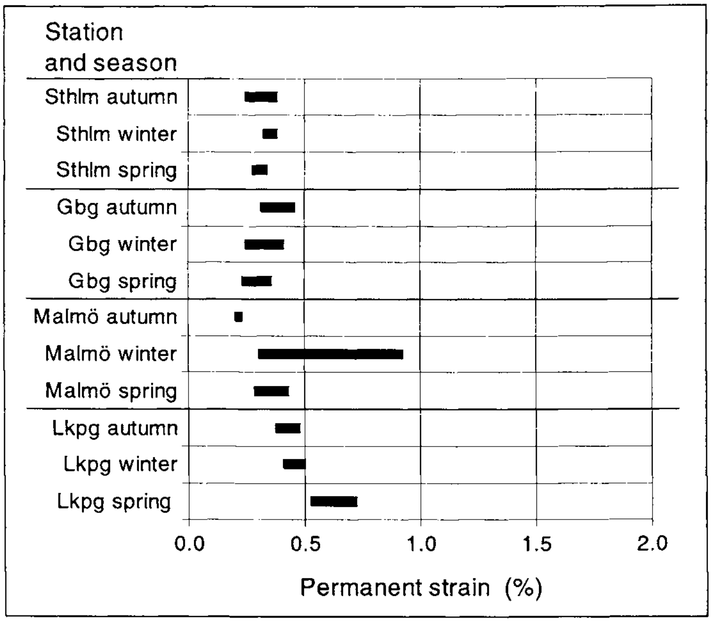


Figure 4. Variation in accumulated axial permanent compression.
5 % significance. Mean normal stress = 50 kPa.

Comparison with conventional materials

The test results have been compared with the corresponding results for natural aggregates that the bottom ash could possibly replace, such as sand with different grading. Those sandy materials were all taken from a construction site, from different sections of the new E6 at the west coast of Sweden. They have been tested in the same way within another research project at VTI (2). In all, it was twelve sandy materials with a sand content between 45 and 91 % and with a water content of ca 0,6 x opt w.

The MSWI bottom ash showed about the same resilient modulus as the sand, but much smaller permanent deformations, see figure 5 and 6.

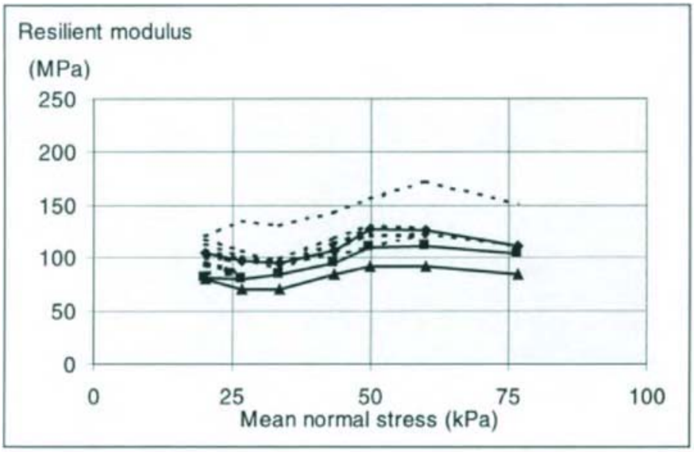


Figure 5. Resilient modulus for bottom ash from Stockholm and different sandy materials. Dotted lines represent sand.

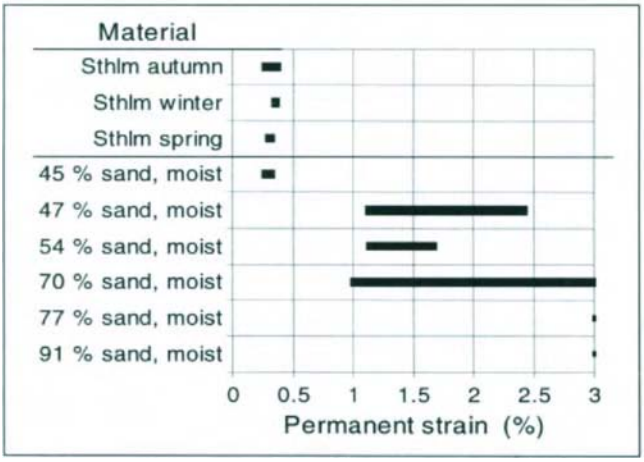


Figure 6. Variation in acc. perm. compression for bottom ash from Stockholm and different sandy materials. 5 % sign. Mean normal stress = 50 kPa.

The fact that the sandy materials showed greater permanent deformations was not surprising since many of the sands were rather even-grained, see figure 7. Nevertheless, they were all "real" material that is being used in road constructions.

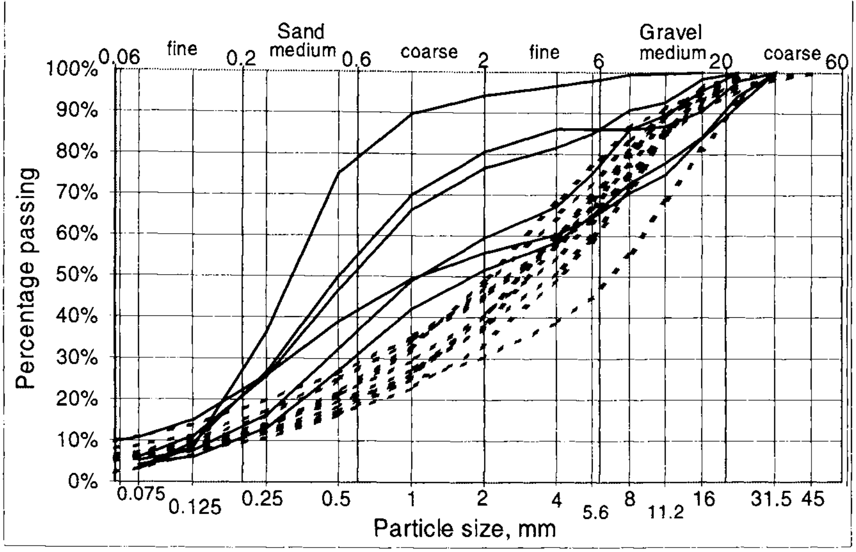


Figure 7. Grain size distribution for twelve bottom ash types and six sandy materials. Dotted lines represent bottom ash.

4. DISCUSSION

Mechanical properties of a pavement layer is very much depending on how well the compaction work has succeeded and this in turn is depending on the grain size distribution and the grain shape of the compacted material. Compaction tool and water supply are other important parameters, but they are no material properties. Furthermore, if the mechanical properties should be kept during the lifetime of the road, the grains must be resistant to both mechanical and climate wear, but that is not discussed in this paper.

A property that is seldom problematic for Swedish conventional road materials, but could be crucial for an incineration bottom ash, is the organic content. Beside the raw material, it is the manufacturing process that controls the organic content and other properties of the ash.

Variations in mechanical behaviour are therefore depending on variation in some or several of the properties mentioned above. These properties are discussed further here below.

4.1. Raw material and organic content

As earlier mentioned, the four incineration stations incinerate both municipal and industrial wastes. The proportions are listed in table 4.

Table 4. (RVF 1997), (from SGI)

Station	Proportion municipal waste	Organic content (LOI)
Stockholm	81 %	3,6-4,2 %
Gothenburg	60 %	2,7-3,7 %
Malmö	59 %	2,6-4,9 %
Linköping	76 %	5,9-9,1 %

According to the table the plants can be grouped into two, namely Gothenburg and Malmö with about 60 % municipal waste and Stockholm and Linköping with ca 80 %. Bottom ash from Linköping has the highest organic content. The ash from this station also turned out to have the lowest stiffness expressed as resilient modulus. An attempt to relate the resilient modulus and the permanent deformation to the organic content has been made in figure 8.

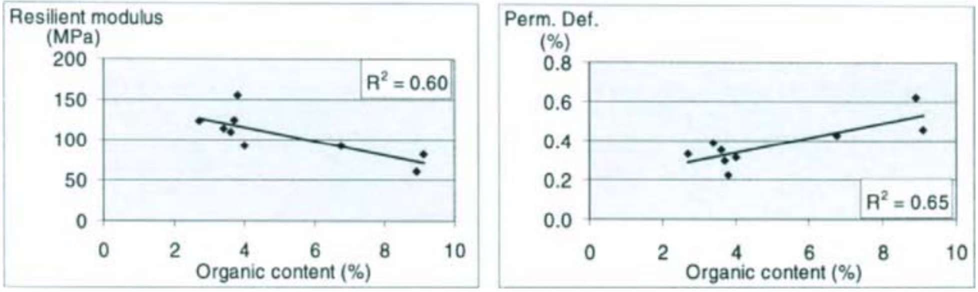
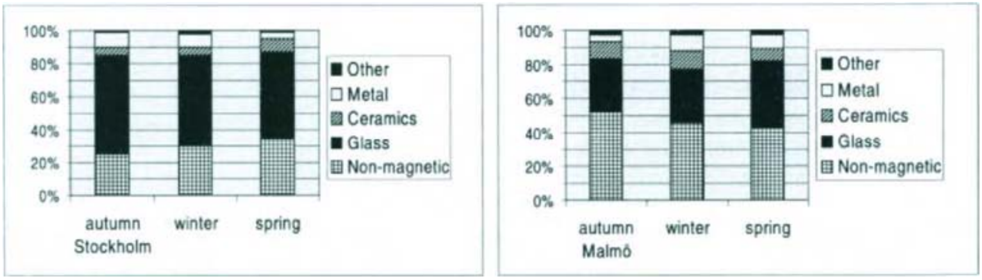


Figure 8. Organic content measured as LOI as a function of resilient modulus and accumulated permanent compression respectively.

It is generally agreed that organic matter has a bad impact on the stiffness. Most country has limited the organic content in road materials. An early Swedish study (3) shows that already a small proportion of organic matter, 6 % of the material with grain size less than 2 mm, deteriorates the E-modulus greatly. The study in this paper suggests that even the permanent deformation is influenced in a negative way.

Also, the material composition has been defined through visual observation. The results are shown in figure 9.



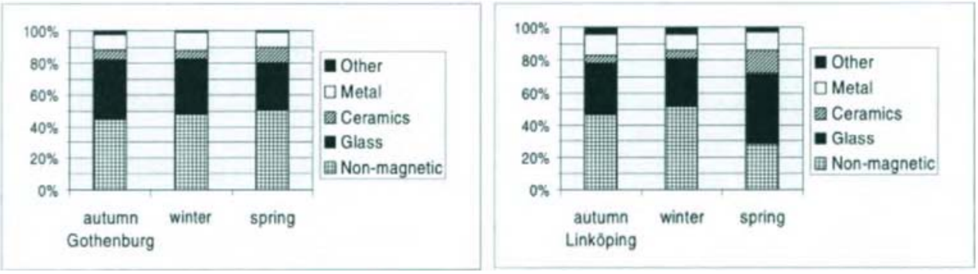


Figure 9. Main constituents of bottom ash from Stockholm, Gothenburg, Malmö and Linköping

From the diagrams it can be seen that there are no great differences between the ashes except for one of the plants, Stockholm, whose ash contains a lot more glass than the other, about 50 % compared to ca 35 %.

4.2. Grain size distribution

In figure 10 the grain size distribution for the ash from each of the studied stations is plotted. The three curves represent material sampled at different seasons.

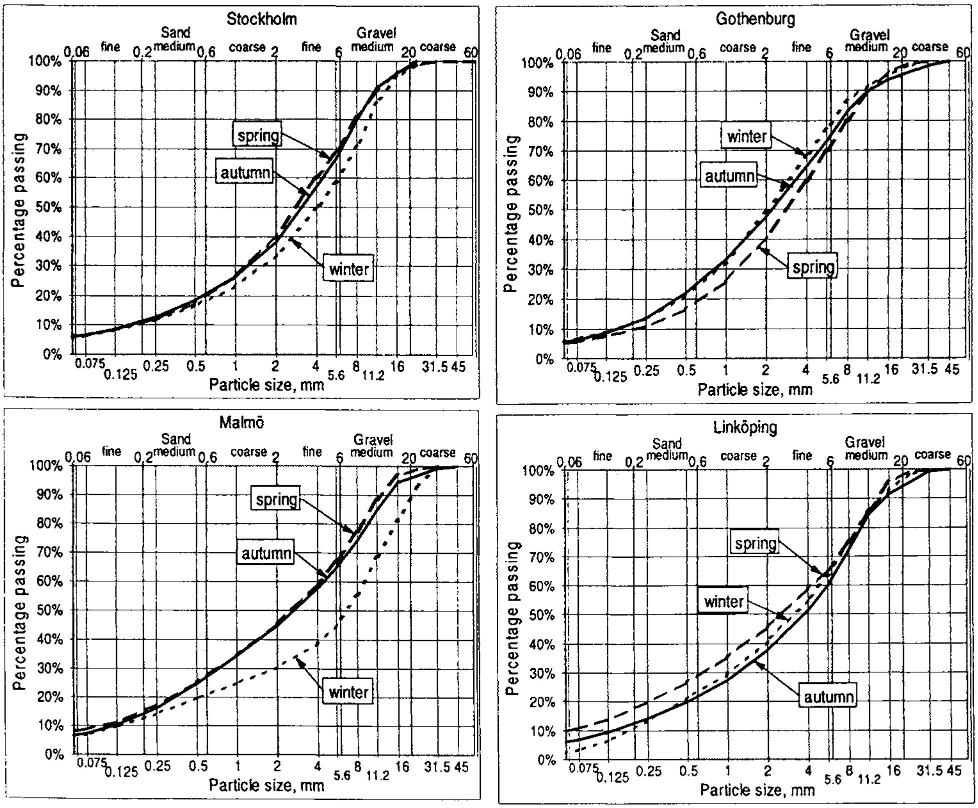


Figure 10. Grain size distribution for studied materials.

According to the grain size distribution all materials can be classified as sandy gravel. It can also be seen that the time dependent variation is small. Even between the stations the differences are small.

Table 5 contains some of the parameters describing the grain size distribution for studied materials.

Table 5. D_{90}, c_u and fines content for studied bottom ash. (autumn, winter and spring ash)

	Stockholm			Gothenburg			Malmö			Linköping		
Season:	a	w	s	a	w	s	a	w	s	a	w	s
d_{90}	11	14	13	13	10	13	14	21	12	15	15	14
c_u	27	32	23	22	21	19	37	68	43	39	26	72
Fines content	6	6	6	6	6	5	7	6	8	6	2	10

Nevertheless, from figure 10 and table 5 a few things can be pointed out.

First, the "winter" ash from Malmö contains more coarse particles (> 6 mm) than the other ashes. This should be favourable for the stiffness.

Second, the "winter" ash from Malmö and the "spring" ash from Linköping have the flattest curve shape. The curve shape can be characterised by a uniformity coefficient, c_u, that is the ratio of d_{60} to d_{10}. D_{60} means the mesh of the sieve through which 60 % of the material pass. For conventional materials, it has been shown that the less steep the curve is, the more stable is the material (2).

Third, the fines content is between 5 and 8 % for all materials with two exceptions, Linköping "winter" with 2 % and Linköping "spring" with 10 %. The fines content allowed in road materials is usually limited because of the risk of frost heave. In Sweden the limit is 8 %. However, a certain amount of fines is essential for a good compaction result.

4.3. Grain shape

The grain shape can be rounded or more or less angular, which has influence on the deformation properties. A more angular material requires a bigger compaction effort, which in its turn can create crushing and an increase of fines. Conversely, a material with rounded particles is generally easy to compact but is also more unstable than an angular material.

Results from another investigation (4) show that MSWI bottom ash has more angular particles than conventional sandy gravel and also more than crushed concrete. It is mostly the particles in the fraction 20–32 mm that are flaky. The content of angular particles could explain the difficulties in compacting the material to laboratory specimens. Field experiences, however, have reported that the bottom ash is very easy to compact (5). This is probably because of the heavy loads that have been used.

4.4. Compaction degree

The fact that the specimens were not tested at the same compaction degree and the same relative water content must be analysed. The 300-mm high specimens with a diameter of 150 mm were compacted in one layer by simultaneous vibration and compression in a Vibrocompresseur. It is a method that has been used with success for conventional materials. Among the advantages can be mentioned that the material is homogeneous compacted and that the water content and density for the specimen can be chosen in advance. Another advantage is that the vibrating compaction is more "friendly" This method was chosen because the modified proctor tests showed a certain crushing tendency for these materials.

However, the target density of 90 % compaction degree was not reached and the water content was above the optimum in all materials except one. The reason for this was probably too angular material and too "careful" compaction. The actual values are given in table 6.

Table 6. Compaction degree (actual dry density/max. dry density from modified proctor tests) and water content for tested materials. Average of three specimens.

	Stockholm		Gothenburg		Malmö		Linköping	
Season	Compact. degree (%)	w (%)	Compact. degree (%)	w (%)	Compact. degree (%)	w (%)	Compact. degree (%)	w (%)
Autumn	84	Opt – 0,5	89	Opt + 1,4	85	Opt + 1,8	86	Opt + 0,8
Winter	87	Opt + 1,0	89	Opt + 0,8	90	Opt + 0,4	88	Opt + 0,7
Spring	88	Opt – 0,1	89	Opt + 0,7	82	Opt + 0,6	80	Opt + 0,8

All the materials from Gothenburg, which had the smallest d_{90} and favourable water contents, were well compacted. They also had resilient modulus above 110 MPa (at a mean normal stress of 50 kPa). Stockholm's "autumn" ash had about the same grain size distribution but was too dry. This is the only material that was tested at a water content below optimum. The compaction degree was therefore considerably lower, 84 % instead of 89%. The resilient modulus for this ash was below 95 MPa.

The different compaction degree and the resulting variation in stiffness show the importance of a good compaction.

5. CONCLUSIONS

The experiments are still going on, but the results so far suggest that the mechanical properties expressed as measured permanent deformation and calculated resilient modulus from triaxial tests are reasonably uniform for each incineration station. There is a significant difference between the stations and even within a station. However, the scatter is not bigger than for the studied natural aggregates.

The value of a relevant design modulus usually depends on where in the construction a material is utilised. Though, it seems that the stress level is not that important for MSWI bottom ash since the tests showed a weak stress dependency for the resilient moduli. From the comparison with some natural aggregates it may be said that if MSWI bottom ash is utilised instead of sand in a capping layer, the same design modulus could be used as for the sand.

All tested materials are stable and give reasonable permanent deformations at the stress level that is relevant for a Swedish capping layer. Furthermore, a better stability expressed as a smaller permanent deformation could be expected if an even-grained sand is replaced by MSWI bottom ash.

It is shown (as expected) that the organic content has a limiting effect on the resilient modulus.

Finally, it can be said that it is possible to create a stiff and stable unbound capping layer of MSWI bottom ash if the organic content is low and the right compaction procedure is used.

ACKNOWLEDGEMENTS

In this research several colleagues at the Swedish Road and Transport Research Institute have taken part. The author wish to express her appreciation for the co-operation, especially to Håkan Arvidsson who did most of the laboratory tests.

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Waste Materials in Construction
G.R. Woolley, J.J.M. Goumans and P.J. Wainwright (Editors)

Self-cementing properties of crushed demolishing concrete in unbound layers

Results from triaxial tests and field tests

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ABSTRACT

A two-year study is underway to evaluate the expected growth in stiffness in layers of crushed concrete from demolishing objects. This growth is said to be a result of self-cementing properties. The study comprises of repeated load triaxial tests on manufactured specimens after different storing time together with falling weight deflectometer, FWD, measurements on test sections. Results so far show a clear increase with time in resilient modulus and in back-calculated layer modulus for all concrete materials. The increase is largest the first months and then diminishes. The field measurements show a more considerable growth in stiffness than the laboratory tests, with a doubled value two years after construction. Comparative investigations on natural aggregates, mostly crushed granite do not show any growth in stiffness, neither in the laboratory nor in the field. Consequences for the choice of design modulus are discussed.

1. INTRODUCTION

Several research projects are going on in Sweden in purpose to facilitate and increase the use of alternative materials in Swedish roads (1, 2, 3, 4, 5). Both design and environmental guidelines are under development. This study deals with the use of crushed demolishing concrete in unbound layers. According to experiences in other countries (6, 7) a growth in stiffness, depending on self-cementing properties could be expected in layers with crushed concrete. The aim with this project was therefore to study the stiffness evaluation in unbound layers of crushed concrete in the laboratory and in the field. Later on, the results will help to establish design manuals where the specific properties of crushed concrete are utilized.

2. METHODS

In the laboratory, the strength properties were studied using repeated load triaxial tests. Complementary properties such as composition, optimum water content and maximum dry density were also investigated. Specimens of crushed concrete from one source, a demolished industrial building in Grums, were manufactured and then tested after different storing time. The specimens were prepared according to the following routine. First, the material was proportioned to a chosen grading, which was a well-graded curve in the centre of the approved zone for base course material in the Swedish guidelines, ROAD 94, (8) as shown in figure 1.

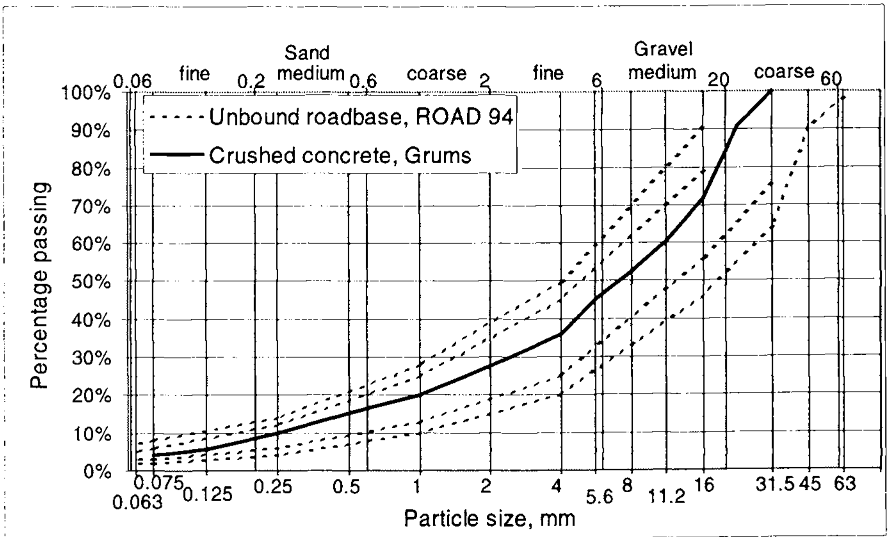

Figure 1. Grain size distribution for material tested in repeated load triaxial tests.

The water content was chosen to 60 % of optimum. Then, 300-mm high specimens with a diameter of 150 mm were compacted, in one layer by simultaneous vibration and compression in a Vibrocompresseur, to 97 % compaction degree. Finally, the specimens were wrapped in plastic folio and stored indoors. After a certain storing time (1, 7, 15, 28, 60, 180, 365 or 730 days) the specimens were exposed to repeated load in triaxial tests and the resilient moduli for different stress conditions were calculated. Comparison with corresponding properties of natural aggregates, such as crushed granite was made.

In the field, test sections with crushed concrete in the sub-base or base course have been constructed at different places in Sweden (9, 10, 11, 12). These are monitored by FWD measurements and for the purpose of this study the layer moduli have been evaluated by means of back-calculation. For comparison, values from reference sections at the same site with natural aggregates in the unbound layers have been used.

The tests are still carried on and will be finished during this year.

3. RESULTS

3.1. Laboratory tests

The material used in the laboratory tests was considered very pure, since more than 95 % consisted of concrete, se figure 2.

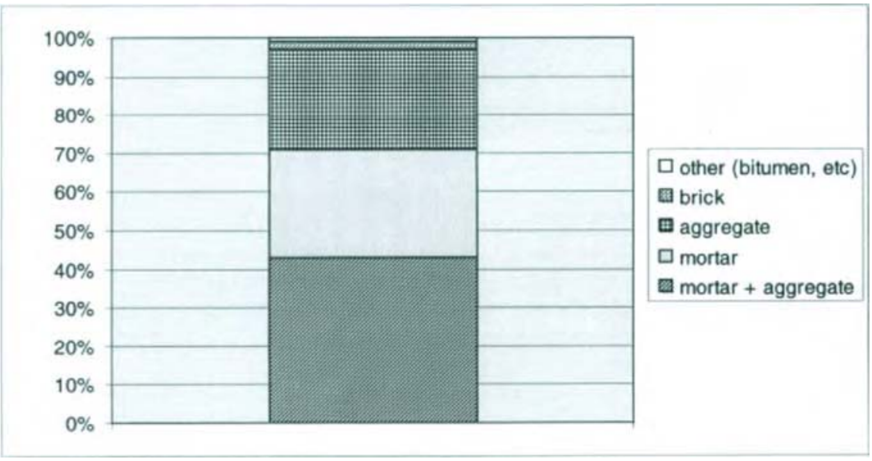

Figure 2. Main constituents of crushed concrete from Grums, weight-% of washed material > 4 mm.

The compaction tests gave an optimum water content for the material of 9.4% and maximal dry density from both modified proctor and vibrator table of 2.0 t/m^3.

In figure 3, the results of the repeated load triaxial tests are plotted as the calculated resilient moduli at different stress conditions. Each point represents the mean value of three specimens. The results will be completed with data from two-year-old specimens, but the tendency so far is a growth in resilient modulus with age.

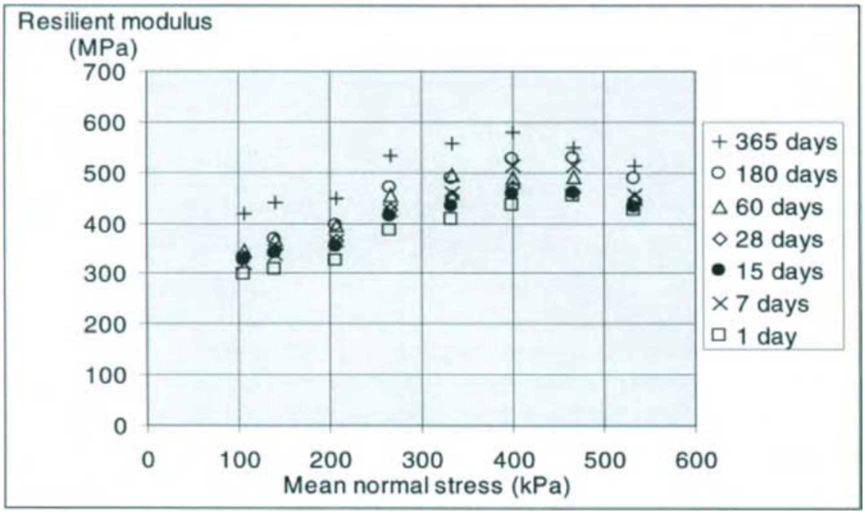

Figure 3. Growth in resilient modulus for crushed concrete from Grums. Results from repeated load triaxial tests after different storing time.

Tests have also been performed on specimens that were stored in wet sand during the first 30 days, since previous Finnish field experiences have shown a positive effect of watering the surface of the concrete layer. Preliminary results, however, suggest a very small increase in resilient modulus for these specimens, which is the opposite of what was expected.

The permanent deformations have not been analysed yet.

Comparison with natural aggregates

The effect of storing time was studied in a small investigation on natural aggregates some years ago (13). In that investigation specimens of crushed and uncrushed granite were tested in repeated load triaxial tests after 1, 3, 7, 28 and 90 days and the resilient moduli were calculated. The results of those tests showed no increase in the resilient modulus, neither for the crushed material nor for the uncrushed material.

Since all the testing parameters and even the grain size distribution were the same for the granite as for the concrete, it is interesting to compare the calculated resilient modulus. In figure 4, values for "fresh" and stored material are plotted and curve fits are made.

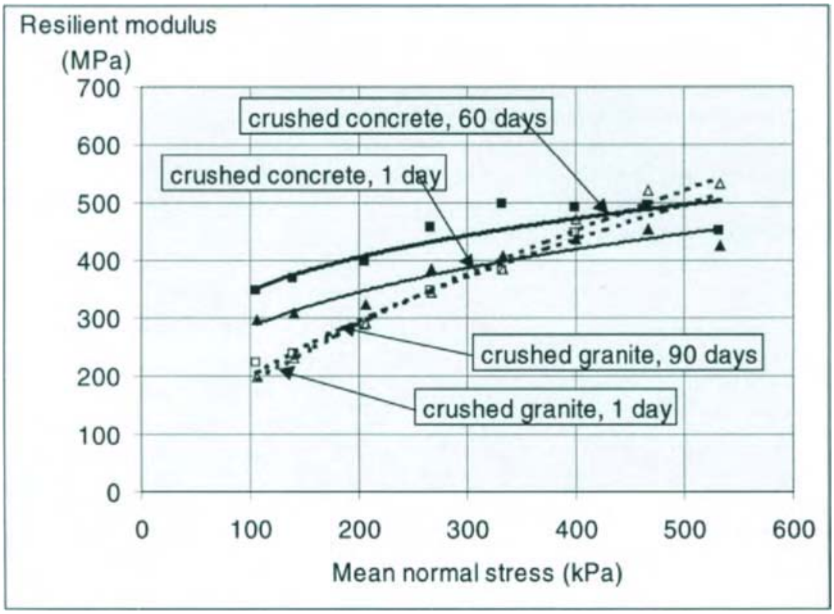

Figure 4. Comparison of modulus change. Resilient modulus from repeated load triaxial tests on granite and concrete.

Two things can be observed. First, the modulus for concrete shows a clear growth at all stress levels, which the modulus for granite does not. Second, the concrete has a less stress dependent resilient modulus than the granite has, which means that at lower stress levels the modulus for the concrete is the highest, while at higher stress levels the modulus for granite is the highest.

3.2. Field tests

Results from FWD measurements at three different sites and at different age after construction are shown in figure 5. In Västerås all the unbound layers consist of crushed concrete (10), while in Björsbyn (11) and in Ekeby it is only the sub-base that contains concrete. Furthermore, at all sites it is concrete from demolished buildings that has been used. It should be noticed that even though it is concrete from different sources, they all have very little impurities, in all cases less than 10 %.

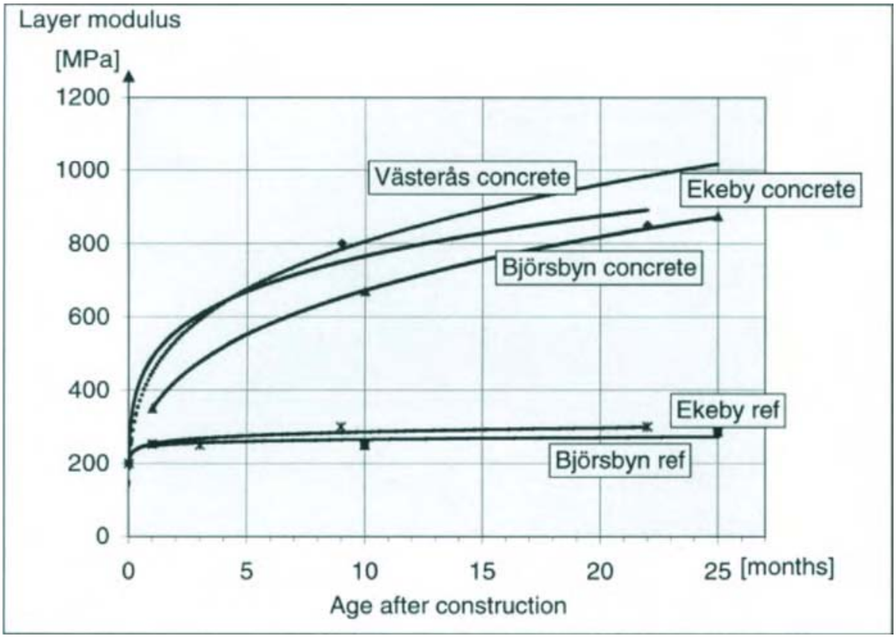

Figure 5. Increase in stiffness. Back-calculated layer moduli for unbound layers of crushed concrete. From FWD measurements

The results from the FWD measurements show a clear growth in layer moduli for the layers with crushed concrete. The growth is largest the first months and then diminishes. The modulus after two years is about twice as high as what is reached after one month.

However, the layer moduli for the unbound layers in the reference sections, do not increase at all or very little during the same period. This results in very big differences in layer modulus between concrete sections and reference sections already after the first months.

4. DISCUSSION

To make use of the self-cementing properties in the design process, there is a need of knowledge of the material stiffness, expressed as a modulus and its growth rate.

Experiences from this study as well as from other laboratory tests at VTI (9, 10, 11, 12, 14) show that crushed concrete from demolishing objects has equal or higher stiffness than natural aggregates, expressed as calculated resilient modulus from triaxial tests. (This is true for lower and medium high stress levels, that is, for stress levels relevant for a Swedish sub-base. The use of crushed concrete in a base course can also be suitable, but not in general, due to the fact that some of the tested concrete materials showed greater sensitivity to high stresses than the natural aggregate did. A fact that is significant in a construction with thin bound layers, where high traffic induced stresses could be expected in the base course.) In figure 6, the results from these triaxial tests, namely resilient moduli for a range of materials, are plotted and curve fits are made. The crushed concrete originates from different sources, such as demolished buildings, a demolished concrete road and railway sleepers. Granite, gneiss and limestone represent the crushed rock. For all materials the grain size distribution, compaction degree and relative water content is the same. The specimens have been tested without previous storing.

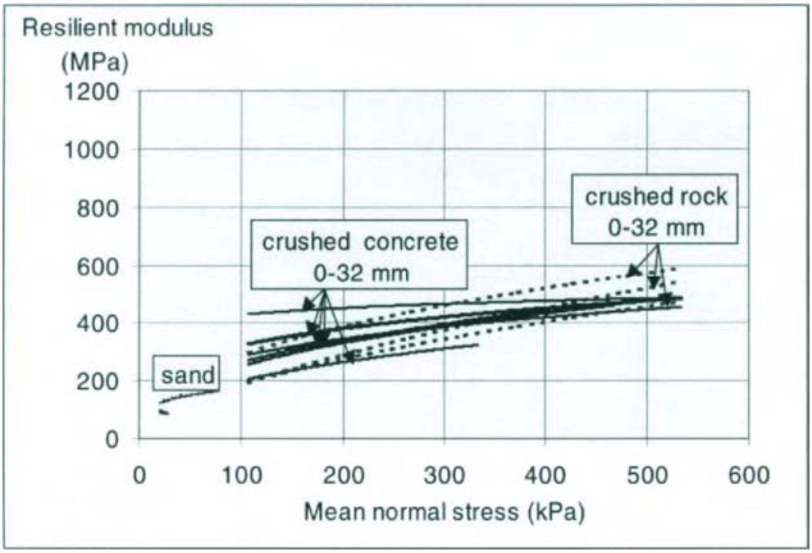

Figure 6. Comparison of stiffness. Crushed concrete and crushed rock with different origin.

There is a certain range in the resilient modulus for different concrete types. However, this is the fact for different rock type also. A more detailed value of the modulus requires an investigation of the specific concrete material and knowledge of the construction that is planned. For example the thickness and type of bound layers have great impact on the stress conditions in the construction.

In this study both laboratory and field results show a growth in stiffness with time, which is not present for natural aggregates. The growth is considerably larger in the field tests than in the laboratory test. The question is how much of the growth that can be taken into account in the design process.

In figure 7, curve fits have been made with equations on the form M = A x (age in months)^B.

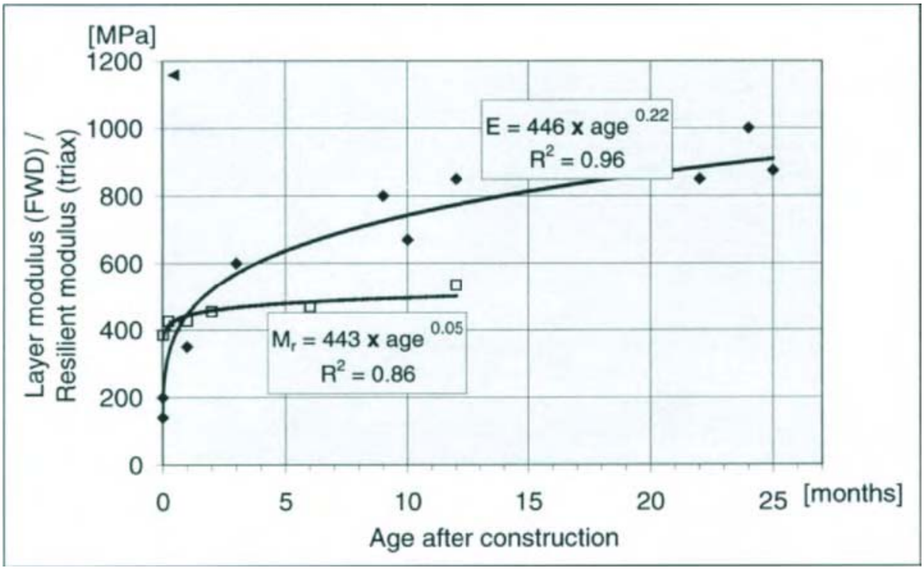

Figure 7. Increase in stiffness. In the field: Back-calculated layer moduli from FWD measurements at three sites. In the laboratory: Resilient modulus for crushed concrete from Grums. Results from repeated load triaxial tests with vertical stress 400 kPa and horizontal stress 120 kPa. Mean value of three specimens.

The field tests gave B values of 0.19, 0.25 and 0.28 for separate sites and 0.22 for all sites together, while the laboratory tests gave the B value 0.05. If, for example, the design modulus should include the increase in stiffness during the first two months, this would give an increase of the start value with (2 months) $^{0.22}$ = 16 % and (2 months) $^{0.05}$ = 4 % respectively. Similarly, the modulus increases with 48 % and 9 % respectively if the value after 6 months is chosen.

However, if the design is made with a modulus value that is reached first after six months, there is a risk that the construction will deteriorate, being "under-designed" the first half year. This can probably be solved during the design or the planning phase.

The analyses and discussions on this subject are continued and will hopefully help to form the base for design manuals for constructions with crushed concrete in the unbound layers. A first step is taken by the guide for recycled crushed concrete as aggregate in roads, which will be published during spring 1999 (15).

5. CONCLUSIONS

In this study, both laboratory and field results show a growth in stiffness for unbound layers with crushed concrete, which is not present for unbound layers with natural aggregates. This growth is considerably larger in the field tests than in the laboratory test. The growth is largest the first months and then diminishes. This means that the layer modulus two years after construction is about twice as high as what is reached after one month.

Even though this is a limited study, some general conclusions can be drawn about the choice of design modulus for crushed concrete. For example, when crushed concrete with very little impurities is used as a Swedish sub-base material, at least the same design modulus can be used as for natural aggregates. However, a special investigation of the specific concrete material, together with knowledge of the planned construction, can give the opportunity to use a higher value on the modulus and by that benefit from the increasing stiffness caused by self-cementing.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

The mechanism of lead (Pb) leaching from incinerator fly ash in monodisposal landfill

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This study considers the leaching behaviour of heavy metals from Municipal Solid Waste Incinerator (MSWI) fly ash contained in a landfill dedicated solely to fly ash disposal. Large scale lysimeters were used to study four materials: untreated fly ash; two types of chemically treated fly ash; and a molten fly ash slag.

The study also considers the effect of highly saline solutions to accelerate the leaching of lead and concludes that the concentration of calcium ions influences the leaching process.

1. INTRODUCTION

There is a growing demand to reduce the volume of organic material that makes up the bulk of waste that is hauled into landfill sites, for the purpose of which many types of pretreatment is conducted. Among the several forms of pretreatment (intermediate treatment) employed is incineration. Incineration results in the enrichment of heavy metals in the residual material (bottom ash and fly ash). In particular, "fly ash" contains high concentrations of lead, cadmium, and other heavy metals, many of which are soluble in water. A number of studies involving leaching tests have been conducted regarding the leaching characteristics of the heavy metals contained in bottom ash and fly ash as part of an effort to utilize incineration residues as construction material. A number of studies have also been conducted regarding the chemical treatment of heavy metals in order to render them insoluble. It is known that the leaching of heavy metals from incineration residues is significantly dependent upon the pH of the leaching solvent [1].

A monodisposal landfill, rather than co-disposal landfill sites, is deemed to afford easier control in order to assure safe disposal and control of harmful substances. However, little is known about the way the leaching of heavy metals from fly ash behaves when treated fly ash is disposed of in a monodisposal landfill site.

In view of this situation, this work examines the outflow characteristics of heavy metals when they are buried in a landfill dedicated to the disposal of incinerator fly ash.

As a general rule, chemicals are used to solidify the heavy metals contained in fly ash, and slag transformation is used to confine harmful substances. Therefore, we have conducted experiments on untreated fly ash, chemically treated fly ash, and molten slag using an outdoor landfill model lysimeter for three years. This paper presents the results of landfill model lysimeter experiments that have been obtained to date. With regard to the phenomenon that the discharge of a high concentration of lead occurred during the initial stages of the experiment when the leachate had high salt concentrations, we also conducted outflow experiments under high salt concentration conditions in order to determine the effects of the kinds of salts present on the rate of lead discharge.

2. LANDFILL MODEL LYSIMETER STUDY

2.1. Landfill Model Lysimeter

Figure 1 shows the landfill model lysimeter that was used in the study. The structure has an inner diameter of 300 mm with a height of 4 m. The rainwater, received through the open top, is collected into a leachate tank at the bottom through water collection pipes. Each lysimeter has a semi-aerobic landfill structure (the most widely used landfill structure in Japan) that permits the inflow of air from the bottom.

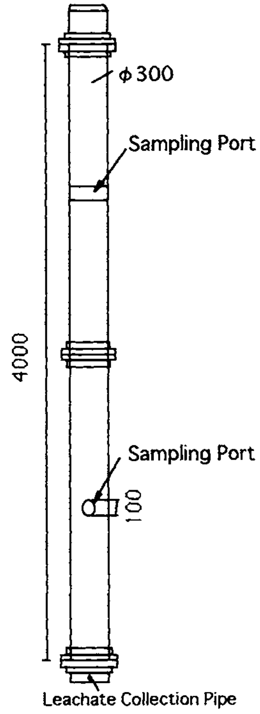

Figure 1. Model Lysimeter

2.2. Samples

The fly ash samples used in the landfill model lysimeter study were obtained by applying various types of treatment to the fly ash discharged from a stoker-type MSWI (dry and wet type gas emission treatment). Untreated fly ash (humidity-adjusted fly ash) and molten slag from the incinerator residues were also studied for controls. Of the experiments conducted using a total of 19 landfill model lysimeters, this paper presents the results in four categories of samples: samples treated with organic chemicals (chelating agents), samples treated with inorganic chemicals (phosphate), untreated fly ash, and molten slag. Table 1 shows the conditions in which the tanks were filled with these materials and their contents.

2.3. Analyses

The total amount of leachate collected was stored and blended. The samples were analyzed after 1, 4, 9, 12, 14, 17, 20, 23, 26, 29 and 35 months for leachate volume, pH, metals (Pb, Na, K, Ca : by ICP), Cl^-, and SO_4^{2-} (by Spectroscopic Analysis).

Table1
Filling Samples

No.	Treatment of Ash	Amount of Sample (kg)	Filling Density (kg/L)	Content Cl^- (g/kg)	Content S (g/kg)	Content Ca (g/kg)	Content Pb (mg/kg)	JLT13 Results Cl^- (g/kg)	JLT13 Results SO_4^{2-} (g/kg)	JLT13 Results Ca (g/kg)	JLT13 Results Pb (mg/kg)	JLT13 Results pH (-)
1	Untreted	257.4	0.900	190	18	260	3300	17	1.1	9.1	95	12.2
4	Organic Chemical	277.2	0.971	200	24	290	2800	17	1.1	8.6	0.09	12.2
8	Inorganic Chemical	311.3	1.095	170	18	240	3300	13	1.5	6.4	<0.05	7.2
11	Molten Slag	383.2	1.341	11	0.1	160	800	0.009	0.016	0.052	<0.05	10.9

JLT13 : Japanese Leaching Test No.13 of the Environment Agency

2.4. Results and Discussion

The dissolution of heavy metals is closely related to the pH of the leachate. Figure 2 shows change in pH of the leachate as a function of time. As indicated in the figure, the fly ash that initially had a pH greater than 10 showed a significant decline in pH between 8 and 9 after 806 days. It should be noted that the fly ash treated with acidic inorganic chemicals (No. 8) initially had a low pH of 4, which gradually increased. The molten slag sample (No. 11) behaved largely in the pH 8-9 zone with the exception of the first month. Figure 3 shows change in Cl^- concentration as a function of time. The chloride ion, which discharged at high concentrations of 250 to 400 g/L, sustained the same condition until the 806th day. By contrast, sample No. 8 showed a declining pattern after 400 days. Figure 4 shows the specific gravities of the leachate samples. Both treated and untreated fly ash samples had a specific gravity of 1.3 or greater from the initial stage of landfill, in which readily soluble inorganic salts dissolved to a near saturation point. The results indicate that the leaching of inordinate amounts of salts can occur when fly ash is buried alone. The reason appears to be the limited amount of rainfall volume relative to the fly ash that is packed in the lysimeter.

Figure 5 shows the lead concentrations in the leachate. The untreated fly ash showed an extremely high initial lead concentration of 3,300 mg/L. The fly ash sample (No. 8) treated with inorganic chemicals temporarily exhibited the discharge of lead at concentrations higher than the lead concentrations observed in untreated fly ash. By contrast, the molten slag did not show any discharge of lead. The lead concentration of the leachate from the fly ash sample treated with organic chemicals was lower when compared with the untreated sample; however, at 8.0 mg/L, it was still two orders of magnitude higher than the 0.09 mg/L leaching value specified by Japanese teaching test No. 13 of the Environment Agency. The reasons for the leaching of lead in such high concentrations appear to be 1) the low liquid/solid ratio (L/S) (L/S = approximately 0.1 after 4 months) compared with the leaching test used in the Environment Agency Circular, and 2) the effects of high salt concentrations.

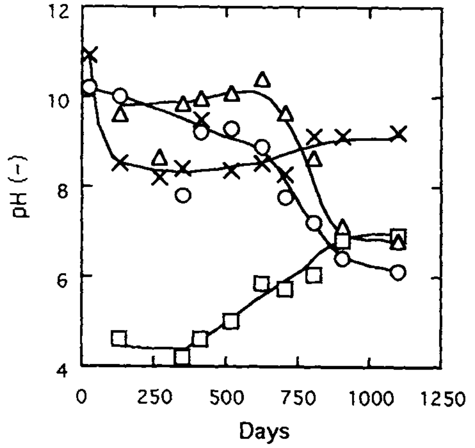

Figure 2. Change pH of Leachate

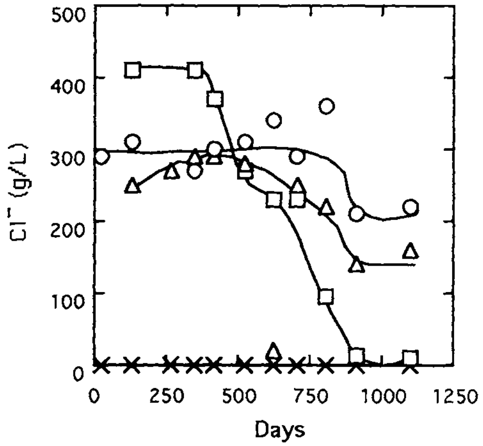

Figure 3. Change Cl^- of Leachate

○ : No.1 (Untreated)
△ : No.4 (Organic Chemicals)
□ : No.8 (Inorganic Chemicals)
× : No.11 (Molten Slag)

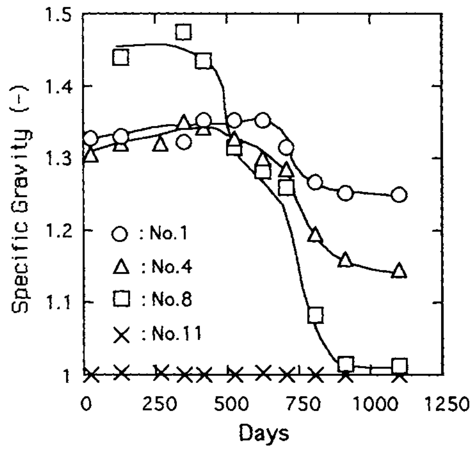

Figure 4. Change Specific Gravity of Leachate

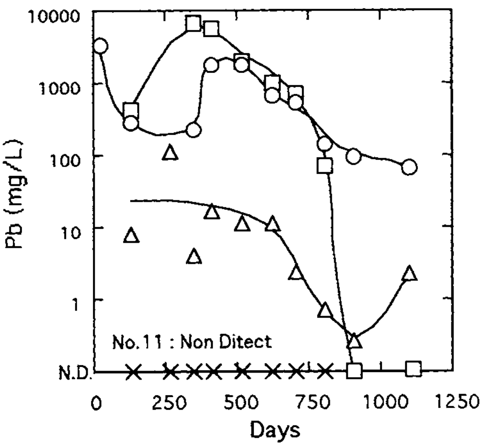

Figure 5. Change Pb concentration of Leacate

O : No.1 (Untreated) Δ : No.4 (Organic Chemicals) □ : No.8 (Inorganic Chemicals) X : No.11 (Molten Slag)

3. LEACHING TESTS under HIGH SALT CONCENTRATIONS

Because it appeared that the initial high concentrations of salts were a contributing factor to the discharge of lead in high concentrations in the landfill model lysimeter tests described above, a study was conducted to verify the leaching of lead under high salt concentrations. A general rule is that the solubility of heavy metals increases under high salt concentrations. The mechanism underlying this behavior is thought to be the predominance of high ionic strength and the formation of salt complexes [2]. In view of this fact, we conducted leaching tests on fly ash under the extremely high salt concentrations that were observed in the landfill model lysimeter studies. Used in this study were the following salts that are considered to be contained in fly ash in high concentrations: NaCl, KCl, and $CaCl_2$.

3.1. Samples

For the incineration fly ash samples for the leaching tests under high salt concentrations, we used the untreated fly ash discharged from a stoker-type Municipal Solid Waste Incinerator (dry type gas emission treatment) that was different from the incinerator used in the landfill model lysimeter study. Table 2 shows the amounts of salts contained in the fly ash and the results of leaching tests.

3.2. Experimental Method

Leaching tests were conducted using a solvent with an adjusted salt concentration and by mixing 100 g of fly ash with 1 liter of solvent in accordance with Japanese leaching test No. 13 of the Environment Agency [3] (L/S ratio: 10; shaking time: 6 hours; filtration: 1 μmGFP). Table 3

Table2 Ash Sapmle Condition

	Contents*	JLT13 Results**
Cl^-	106	11.2
SO_4^{2-}	42	2.43
Ca	18.7	3.77
Pb	1560	25.4

*Unit : Cl^-, SO_4^{2-} (g/kg), Pb (mg/kg)

**Unit : Cl^-, SO_4^{2-} (g/L), Pb (mg/L) shows the concentrations of salts in the solvent that was used in the experiment. The following salts were used in a concentration range of 1 g/L to 150 g/L: NaCl, KCl, NaCl + KCl, and $CaCl_2$. The maximum Cl^- concentration that was set was somewhat lower than the leachate chloride concentration observed in the landfill model lysimeter test.

Table3 Solvent Condition of Leaching Test

Cl^- conc.(g/L)	NaCl add	KCl add	NaCl+KCl add	$CaCl_2$ add
1	○	-	-	-
2	○	-	-	-
10	○	-	-	○
20	○	-	-	○
50	○	○	○	○
80	-	-	-	○
100	○	○	○	○
150	○	-	-	-

3.3. Measurement Species

Leachate obtained from the leaching test were analyzed for pH and for the concentrations of Cl^-, SO_4^{2-}, Na, K, Ca, and Pb.

3.4. Results and Discussion

Figure 6 shows the pH values of the Leachate obtained. The pH values, ranging from 11.7 to 12.6, showed little difference from one type of solvent to another.

Figure 7 shows the concentrations of lead in solvents in which NaCl and KCl were added. The concentration of lead tends to decline as the concentration of Cl^- rises. An increase in Cl^- concentration alone does not increase the concentration of lead. Figure 8 shows the concentrations of lead in a solvent to which $CaCl_2$ was added, wherein the concentration of lead increased proportionally to the concentration of Cl^-. At the same time, there was a significant decrease in the concentration of SO_4^{2-} in the leachate, which suggested the occurrence of an ion exchange reaction due to the presence of both $PbSO_4$ and $CaSO_4$ as follows:

$$PbSO_4 + Ca^{2+} \rightarrow CaSO_4 + Pb^{2+}$$

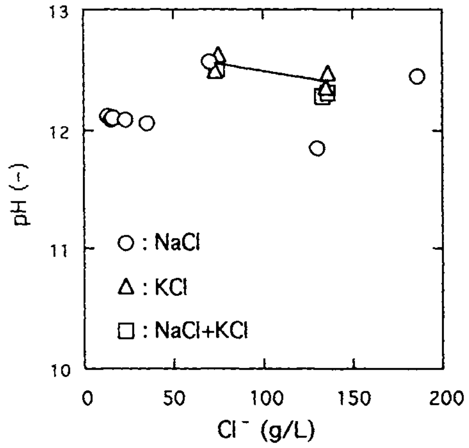

Figure 6. Change pH by Cl^- conc.

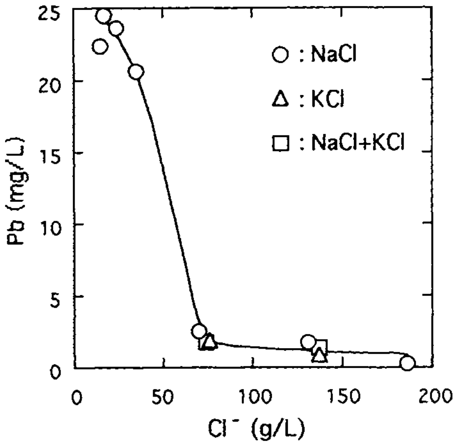

Figure 7. Change Pb conc. by Cl^- conc.

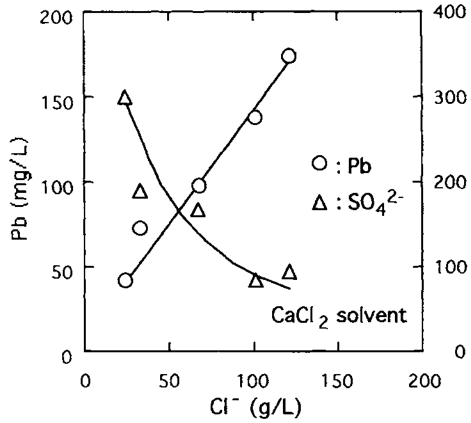

Figure 8. Change Pb conc. and SO_4^{2-} conc. by Cl^- conc.

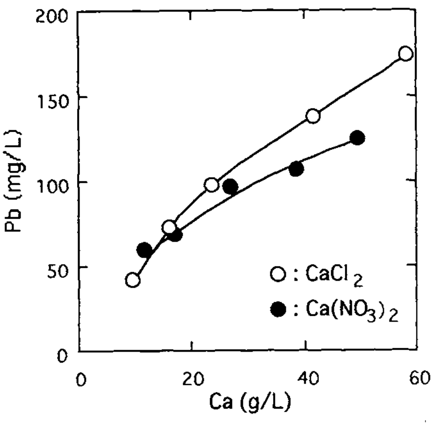

Figure 9. Ca conc. vs Pb conc. in solution

These results parallel the phenomena observed by Shinagawa *et. al.* in a study using pure chemicals [2].

Because it was determined that the calcium concentration influences the concentration of leached lead, a leaching test was conducted by varying the Ca concentration stepwise (10, 15, 25, 40, 60 g/L) and by using an aqueous solution of $Ca(NO_3)_2$, which is an easily soluble compound of calcium not containing Cl^-. Figure 9 shows the concentration of lead when aqueous solutions of $CaCl_2$ and $Ca(NO_3)_2$ are used as solvents. The Pb concentration reached 174 mg/L under high salt concentrations (Cl^-: 120 g/L; Ca: 59 g/L). This was 5 times greater than the value, 25.4 mg- pb/L, indicated in Japanese leaching test No 13 of the Environment Agency. In terms of solvent types ($CaCl_2$ vs. $Ca(NO_3)_2$), there was relatively little difference in Pb concentration when compared with the case of solvents containing high salt concentrations. Because NO_3^- has virtually no influence on the solubility of Pb, it appears that the concentration difference due to the use of different solvents is attributable to the formation of a salt complex. It appears that at a calcium concentration of 50 g/L, 80% of the increase in Pb leaching concentration is attributable to Ca and the remaining 20% to the influence of Cl^-. It can also be postulated that in the low salt concentration region the presence of Cl^- exerts little effect on the leaching of lead.

In the future, it will be necessary to study in detail the specific compounds in which lead exists on the surfaces of fly ash particles when they have come into contact with water.

4. SUMMARY

Following is a summary of information obtained from landfill model lysimeter studies and from the results of leaching tests conducted under high salt concentrations:

1) When fly ash is buried on a monodisposal basis, extremely high concentrations of lead and salts discharge for approximately one year from the time it was buried.

2) It appears that the presence of a high concentration of salts in landfill leachate accelerates the leaching of lead from the fly ash.

3) During the experimental period, no appreciable amount of lead leached from molten slag.

4) Leaching tests conducted under high concentrations of salts indicate an increase in lead concentration in proportion to the concentration of calcium.
5) It appears that the mechanism responsible for the promotion of leaching of lead from the fly ash under a high concentration of calcium is an exchange reaction that occurs in the presence of both $PbSO_4$ and $CaSO_4$ due to a change in the concentration of Pb and SO_4^{2-} leaching from the fly ash.
6) The results of leaching tests conducted using two types of calcium compounds indicate the calcium concentration has a greater impact on the leaching of lead from the fly ash when compared with the concentration of Cl^-.

There is an opinion that, from the standpoint of managing the risks associated with the toxicity of incineration fly ash, fly ash should be buried in monodisposal landfill sites. However, the experimental results presented herein indicate that, when buried on a monodisposal basis, fly ash is prone to discharge heavy metals, which carries a hazard that must also be considered.

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Heavy metal elution characteristics from municipal solid waste scrubber residue by a centrifugation method

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The objective of this study is to clarify the elution characteristics of heavy metals into scrubber residue solution such as bound water and pore water. The L/S ratio of wet scrubber residue is smaller than that the L/S ratios used in elution tests such as: the one based on Notification No.13 of the Japanese Environment Agency (Japanese official method,JLT13), the Toxicity Characteristics Leaching Procedure (U.S.A. official method) and the Availability test (Dutch official method). A centrifugation method employed to sample soil solution was adopted for use to sample two types of scrubber residue solutions, and to compare the concentrations of heavy metals in the leachates with that obtained from the JLT13 and the Availability test as well as the pH dependency test.

1. INTRODUCTION

The elution characteristics of heavy metals from the municipal solid waste scrubber residue have been studied by elution tests such as: the one based on Notification No.13 of the Japanese Environment Agency (Japanese official method, JLT13), the Toxicity Characteristics Leaching Procedure (U.S.A. official method, TCLP) and the Availability test (Dutch official method). The liquid-solid ratios (L/S ratios) of these test methods are different from one another; they are 10, 20 and 100, respectively. These tests do lend themselves to predicting composition in scrubber residue solution such as the bound water and the pore water in wet scrubber residues; this is a concern for management of leachate from landfills in Japan.

The objective of this study is to clarify the elution characteristics of heavy metals in the scrubber residue solution. The L/S ratio of wet scrubber residue is smaller than that those used in elution tests. Because of the differences in these L/S ratios, the qualities of waters around scrubber residues (e.g. water retained by wet scrubber residue and leachates in elution tests) are considered to be greatly different.

Scrubber residues disposed of in landfills are wetted. To predict the properties of leachates from landfills, it is more useful to investigate the quality of scrubber residue solution (bound water and pore water) directly. This will provide information on water quality closer to that of actual field leachates.

From these viewpoints, a centrifugation method employed to sample soil solution was adopted for use to sample scrubber residue solution, and to compare the concentrations of heavy metals in the leachates with that obtained from elution tests such as the JLT13, the Availability test and pH dependency test, thereby clarifying the elution characteristics of heavy metals from the scrubber residue of municipal solid waste.

2. SAMPLE AND EXPERIMENT METHOD

In the experiment using the centrifugation method, we employed two types of scrubber residues (scrubber residues A and B) sampled from two municipal solid waste incineration plants. Both types of scrubber residues are based on stoker furnaces and dry exhaust gas disposal methods. Table 1 shows the compositions of the two scrubber residues.

Table 1
Scrubber Residue Composition

Unit : mg/kg

Component	Scrubber Residue	
	A	B
Cl^-	87,000	166,000
Ca	207,000	311,000
Na	38,100	56,400
K	34,000	53,300
Mg	15,000	10,000
Al	75,000	29,000
Fe	48,000	7,700
Zn	9,100	4,800
Pb	2,080	1,610
Cu	50	390
Mn	4,600	150
T-Cr	260	70
Cd	83.0	43.4
As	10	6
Se	0.2	0.2

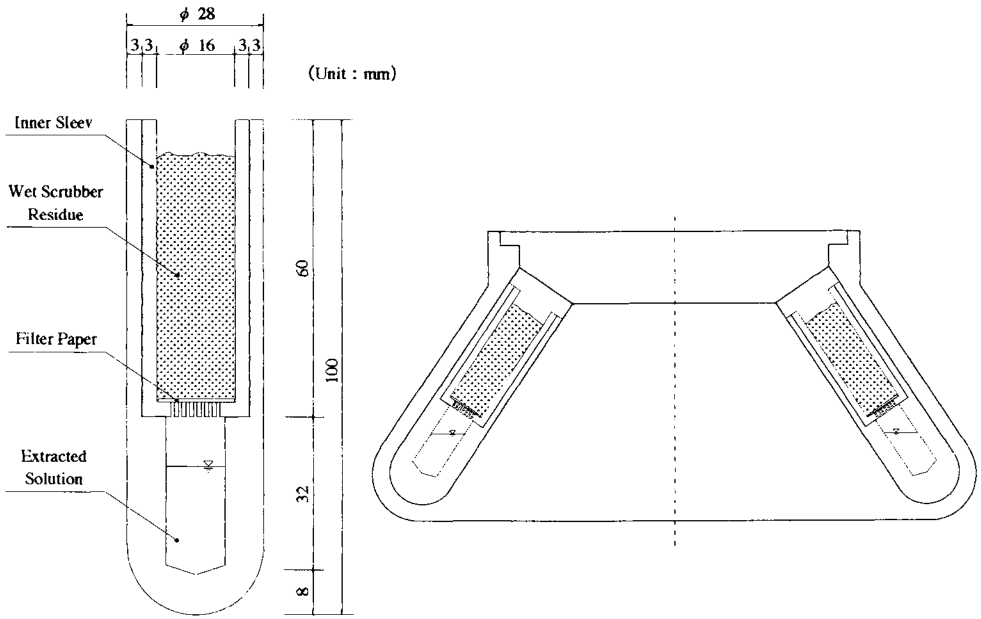

Figure 1. Rotor and Centrifugation Tubes

In the experiment, we added distilled water to scrubber residues in order to ensure the specified water contents (L/S ratios), and mixed them sufficiently to make them uniform. After that, to ensure uniform wet condition of scrubber residue, we used wet scrubber residues left standing at room temperature for 24 hours. We sampled scrubber residue solutions that were produced using a general-purpose centrifuge.

Figure 1 shows the rotors of centrifuge and the centrifuge tube. This rotor accommodates eight tubes. The centrifuge tube is a custom-designed product and is configured in a special structure comprising outer and inner sleeves. Fine holes are provided at the bottom of the inner sleeve. The inner sleeve is filled with the wet scrubber residue, and dewatering is made by centrifugation at a specified rotational rate between 1,000 rpm and 10,000 rpm. The extracted solution collects on the bottom of the outer sleeve.

We analyzed the metals and salts contents in the scrubber residue solutions and in the leachates from the JLT13 (shaken for 6 hours at the L/S ratio of 10 with distilled water used as solvent), the Availability test and the pH dependency test using atomic absorption spectrometry.

In the analysis of heavy metals in the scrubber residue solutions and leachates in the elution tests, we used the material filtered by 1.0μm (for the JLT13) or 0.45μm (for the centrifugation method, the Availability test and pH dependency test) membrane filters.

3. RESULT OF EXPERIMENT AND DISCUSSION

3.1. Application of Scrubber Residues to Centrifugation Method

Figure 2 shows the relationship between the mass of extracted solution by the centrifugation method from the wet scrubber residue A in the centrifuge tubes and time of duration of centrifugation. Each centrifuge tube was filled with 17.0 g (a total of 136.0 g in

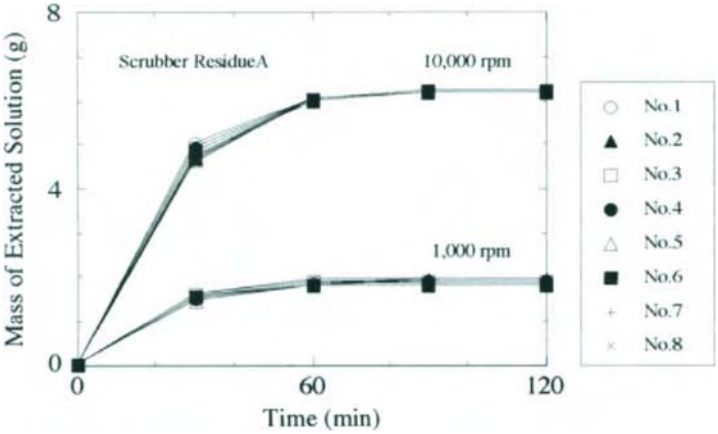

Figure 2. Relationship between the Mass of Extracted Solution and Centrifugation Time

Table 2

pH and Pb for Eight Scrubber Residu solutions

Rotation Rate (rpm)	pH (-)		
	Min.	Max.	Ave.
1,000	11.0	11.1	11.1
10,000	11.1	11.2	11.2

Rotation Rate (rpm)	Pb (mg/L)		
	Min.	Max.	Ave.
1,000	151.3	169.5	160.6
10,000	202.8	234.8	222.1

* Scrubber Residue A

eight centrifuge tubes) of wet scrubber residue. The initial water content in wet scrubber residues was 41.1 % (= L/S 0.70) at the rotational rate of 1,000 rpm, and 42.7% (= L/S 0.75) at the rotational rate of 10,000 rpm. In approximately 90 minutes, independent of the rotational rate, there were no further changes in the mass of extracted solution. The extraction rate was about 26 % at the rotational rate of 1,000 rpm and at the rotational rate of 10,000 rpm is about 85 %. Variations between centrifuge tubes were very small. There were almost no variations in the masses of extracted solution among centrifuge tubes at 10,000 rpm. From these observations, we determined the optimum settings for centrifugation were 90 minutes at 10,000 rpm.

Table 2 shows the pH and Pb for eight scrubber residue solutions. The pH was not affected by rotational rate, and there was small variation. The coefficient of variance (CV) was 0.10. However, scatters were observed in Pb concentration among centrifuge tubes. The difference of 6 to 9% was observed between the arithmetic mean value and the maximum/minimum values. The CV was 0.94 at the rotational rate of 1,000 rpm, and 0.96 at the rotational rate of 10,000 rpm. Thus, in a series of studies, all the solutions sampled in eight centrifuge tubes were mixed and the total mass of extracted scrubber residue solution was used as one sample for further analysis.

3.2. Properties of Scrubber Residue Solution and Leachate in the Elution Tests

Table 3 shows the concentrations of components in the leachates gained from the elution test based on the JLT13 and in the scrubber residue (scrubber residue B) solutions obtained from the centrifugation method. We conducted similar experiments on not only the wet scrubber residue, but also on the treated scrubber residue by phosphate for heavy metals stabilization. Water content at the time of dewatering by centrifugation was 60.0 % (= L/S 1.5) for the scrubber residues of both cases.

We compared the concentrations of many components in the scrubber residue solutions extracted by the centrifugation method and leachates by the JLT13. The concentration of components detected in untreated scrubber residue solution is higher in the centrifugation method by one order or more orders of magnified. Furthermore, some metals (Mg, Mn, Cr and Cd) not detected in the JLT13 (below the limit of determination) were detected according to the centrifugation method. Scrubber residue solutions contain high concentrations of salts. While concentration of the salts (a total of Cl^-, Ca, Na and K) in the JLT13 leachate was about 32 g/L, that of the scrubber residue solution was about 380 g/L. Salts in the scrubber residue solution are considered to be close to saturation. For metals, high concentrations of Pb, Zn and Fe were detected in the solutions. The L/S ratio was 10 in the JLT13, while the L/S ratio in the centrifugation method here is 1.5. In the scrubber residue solution, there are many components which exhibit a higher concentration than that calculated from both L/S ratios (10/1.5=6.7). The Cl^- concentration in the untreated scrubber residue in the centrifugation method shows the concentration about 12 times that in the JLT13. Similarly, the Pb concentration is about 50 times higher in the centrifugation method.

The effects of phosphate treatment reduced heavy metal leaching so that little differences were seen in the JLT13 and the centrifugation method. This shows that heavy metals are made stable by phosphate. These data suggest that the centrifugation method can be a new test method for more precise understanding of the effect of treatment of scrubber residue by chemicals, and of the small L/S ratio (low water content) of wet scrubber residue

Table 3

Properties of Leachate in the Elution Test and Solution

Unit : mg/L

Component	Untreated Residue		Treated Residue	
	JLT13	Centrifugation	JLT13	Centrifugation
pH	12.0	10.8	12.0	10.3
Cl^-	17,500	217,000	12,600	217,000
Ca	6,330	60,300	4,490	49,800
Na	4,520	56,600	2,760	61,200
K	3,810	43,500	2,690	56,600
Mg	< 0.1	0.3	< 0.1	0.1
Al	< 0.1	< 0.1	< 0.1	< 0.1
Fe	0.4	16.4	0.2	4.4
Zn	2.6	38	0.4	4
Pb	7.68	392	0.39	73
Cu	0.4	1.2	0.1	0.6
Mn	< 0.1	0.8	< 0.1	0.8
T-Cr	< 0.2	1.7	< 0.2	0.9
Cd	< 0.01	0.24	< 0.01	0.07
As	< 0.01	< 0.01	< 0.01	< 0.01
Se	< 0.01	< 0.01	< 0.01	< 0.01

* Scrubber residue B, ** After 1 day, 10,000 rpm

such as of in a landfill.

3.3. Comparison of the Elution Mass of Components

We then examined the relationship between the mass of elution of heavy metals from the scrubber residues according to the centrifugation method and the mass of elution obtained from Availability test and pH dependency test and the heavy metals content of the scrubber residue. Figure 3 shows the mass of Pb elution as well as its content per unit mass of scrubber residues according to each elution test method. In calculation of the mass of elution according to the centrifugation method, dehydrated solution accounts for about 80 % of the volume of water added to the scrubber residue (see 3.1.). This was multiplied by water volume added to Pb concentration of the scrubber residue solution dehydrated by the centrifuge, and the result of this multiplication was determined to be the mass of elution according to the centrifugation method. The mass ratio of Pb elution to the Pb content was about 33 % in the case of scrubber residue A according to centrifugation method, and about 7 % in the case of scrubber residue B. According to the Availability test, by contrast, it was 22% in the case of scrubber residue A and 5% in the case of scrubber residue B.

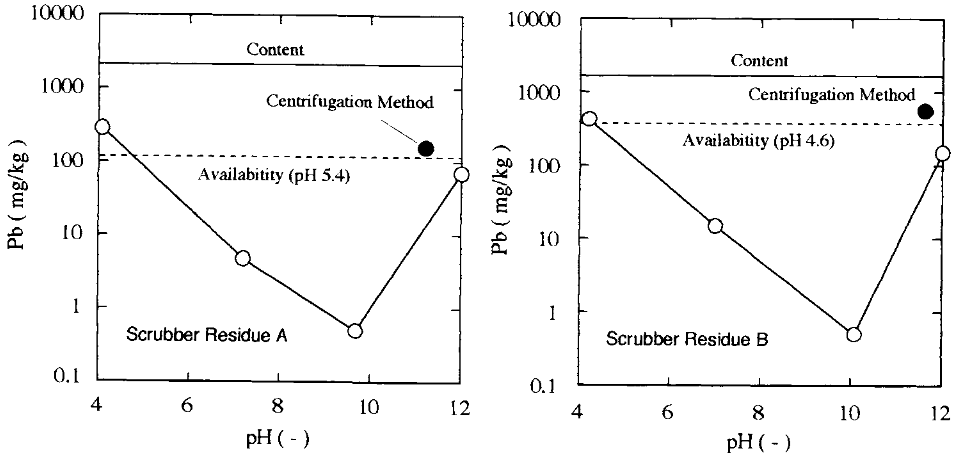

Figure 3. Comparision of Elution Mass of Pb

In the pH dependency test, the mass of Pb elution obtained in the range from pH 4 to 12 was smaller than that obtained by the centrifugation method or the Availability test, except in the low-pH range. The final pH value in the Availability test should be 4.0. However, in this experiment, the pH value of scrubber residue A was 5.4 and that of scrubber residue B was 4.6. This is higher than the specified pH value 4.0. So the mass of elution obtained in the Availability test is smaller than that at the minimum pH in this pH dependency test.

Even when these facts are taken into consideration, the mass of Pb elution in the centrifugation method is equal to or greater than that gained in the Availability test, even if the pH of the solution is not very high (pH 11.2 for scrubber residue A and pH 10.6 for scrubber residue B).

The reason why Pb in scrubber residue solution exhibits such a high concentration may be the ion strength or generation of chlorine complex, since the solution showed a very high concentration of salts. For Pb, the substitution reaction between Ca and Pb in the coexistence of $CaSO_4$ and $PbSO_4$ at a very high concentration of inorganic salts is also involved in explaining this phenomenon, according to the information gained in our separate research projects [1].

3.4. Impact of Rotational Rate upon Solution Quality

Water with different retentivities (e.g. pore water in fine and coarse pores, weakly bound water and strongly bound water) is considered to be recovered by changing the rotational rate of the centrifuge, namely, the centrifugal force acting on the wet scrubber residues. So we determined to sample the scrubber residue solution by changing the rotational rate and to get the relationship between the concentration of Pb in solution and the rotational rate. The centrifugation time was 90 minutes. In this experiment, we also made tests by changing the contact period (for 0, 1 and 3 days) of distilled water and the scrubber residues. The initial water content was 42.1 % (=L/S 0.73) for scrubber residue A and 36.1 % (=L/S 0.66) for scrubber residue B. The amount of water evaporated from the wet scrubber residues during the period of leaving the sample was gained by measuring the mass

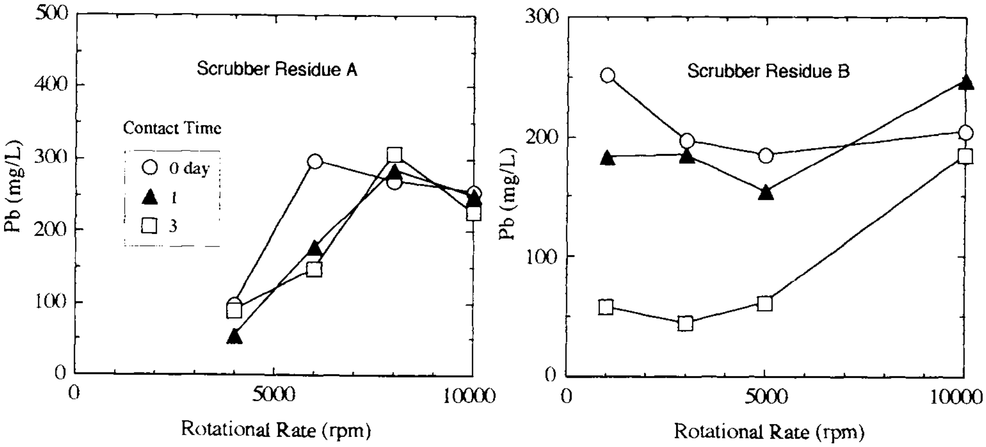

Figure 4. Impact of Rotation Rate upon Solution Quality

of the samples. We made up for the daily loss in the mass of water.

Figure 4 shows the results for scrubber residues A and B. The concentration of Pb obtained in the scrubber residue solution tended to be higher as the rotational rate (centrifugal force) was greater. This is especially conspicuous from 4,000 rpm to 8,000 rpm for scrubber residue A, as shown in Figure 4. The Pb concentration at the rotational rate of 8,000 rpm is three times that at the rotational rate of 4,000 rpm. We changed the rate in the low rate range (1,000 to 5,000 rpm) for scrubber residue B, but a clear correlation was not observed between the Pb concentration and the rotational rate. This observation suggests that a higher concentration of Pb is dissolved in water present in the vicinity of scrubber residue particles (bound water) than in water present in the fine and coarse pores created by scrubber residue particles (pore water). It can be inferred that a higher concentration of inorganic salts is dissolved in water present closer to scrubber residue particles. This is estimated to have an impact on the elution of Pb. To clarify the phenomena exhibited in this experiment in the future, it is necessary to find out the form of water retained in scrubber residues (for example, water content characteristics curve pF), pH and Eh of bound water and pore water, and concentration of other solved components such as salts.

Lastly, it is important to understand the effects of contact time on elution characteristics. Independently of time, the concentration of Pb obtained in the scrubber residue solution tended to be higher as the rotational rate was greater. Furthermore, the concentration of Pb in the solution tended to be lower as contact time increased. The Pb dissolved from the scrubber residues is considered to have been made insoluble. The same phenomenon as the aging effect (Pb insolubility) of the wet scrubber residues in the elution test such as JLT13 test 2) was observed in the concentration of Pb in scrubber residue solutions.

4. CONCLUSION

This study was conducted to clarify elution characteristics of heavy metals into scrubber residue solution such as bound water and pore water in wet scrubber residue. Using two types of scrubber residues, water retained by wet scrubber residues was extracted by the centrifuge to get the solution and the properties of it. We also compared the properties of the leachates obtained from the JLT13 and the Availability test as well as the pH dependency test to clarify the following points:

(1) It was possible to extract the solution retained in the wet scrubber residue (with water content between 40 and 60 %) by the centrifugation method using a general-purpose centrifuge. We could extract the scrubber residue solutions at the rotational rate of 10,000 rpm over 90 minutes.

(2) A very high concentration of metals (Pb, Zn and Fe) and salts (Cl^-, Ca, Na and K) were observed in the scrubber residue solution. The solution contained salts having a concentration close to saturation. Concentration of each component in the scrubber residue solution was higher by one order or more than the concentrations observed in leachates from the JLT13 (official elution test in Japan). Furthermore, the concentrations of Mg, Mn, Cr and Cd that were below the limit of detection according to the JLT13 were detected in the centrifugation method.

(3) The mass of Pb extracted from the scrubber residues in the centrifugation method was almost the same as that in the Availability test (official elution test in Holland).

(4) In the centrifugation method, Pb concentration in scrubber residue solution tended to increase as the rotational rate increased.

(5) The aging effect of wet scrubber residues confirmed in the leachate of the elution test has also been confirmed in scrubber residue solution according to the centrifugation method.

Compared with the existing solution test methods, the centrifugation method is considered as a test method which provides a simpler means to examine elution characteristics of heavy metals from scrubber residues and scrubber residues subjected to stabilization treatment in a shorter time. We are planning to establish the centrifugation method for scrubber residues. We are also thinking of examining the feasibility of predicting the quality of leachate according to the centrifugation method through comparative studies between the quality of scrubber residue solution obtained in the centrifugation method and that of leachate from the landfill or the column filled with scrubber residues.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Requirements for a Realistic Estimate of the Source Term for Heavy Metal Elution from Mineral Wastes

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Several toxic high volume mineral wastes which are disposed of in Germany in underground facilities in former salt mines have been subjected to a variety of leaching tests (DEV S4, column elution test, cascade test) with respective geological solutions. The objective was to check the aptitude of these tests to predict the long term leaching behaviour in case of water intrusion into the salt mine. Most insight into the reaction pathway is gained by the cascade test in which solid-fluid ratios of 3 to 8 (kg/kg) can be reached which are representative of underground disposal facilities. As cost would render this test unacceptable as a compliance test, model calculation may bridge the gap since good agreement was observed with experimental data from cascade tests. Indispensable parameters are the elemental contents of the waste and their individual leaching rates which in many cases can be determined by single day elution tests such as the DEV S4.

1. INTRODUCTION

A great number of leaching tests, like single-step and multi-step extraction tests, column elution tests and cascade tests have been developed in the last years for different applications like soil clean-up, sludge treatment, use of secondary materials in construction and waste treatment and disposal. In general, the objective of such tests is to gather information on the mobilisation of toxic ingredients from the solid material when it comes into contact with a leaching fluid. The potential as well as the shortcomings of such standard tests have been analysed in many careful investigations and reviewed [1].

In Germany, the DEV S4 standard test [2] is routinely applied by waste producers as compliance test. This test was originally devised for studying the leaching of toxic ingredients from sediments and sludges in the case of above ground deposition. Nonetheless, the DEV S4 test is also applied to toxic waste which is disposed off underground in former salt mines, although the test parameters do hardly represent the boundary conditions of deep disposal. Mobilisation of toxic waste ingredients can potentially occur upon post-operational water intrusion into a former salt mine. Since a high ionic strength solution would result, the use of solutions which are representative of the geological situation as eluents in DEV S4 tests (instead of distilled water) has been officially endorsed. One potential shortcoming of the DEV S4 test is associated with the short leaching time which may prevent equilibrium between solution and solid material being fully established, so that extrapolation of the results to the very long time frame of underground disposal may be erroneous.

Another important aspect concerns the mass relation between the leaching solution and the solid material. In most extraction tests, especially in serial batch tests, high solution volumes compared to the amount of solid are used, hence, the leachate-solid ratio (l/s ratio) has been established as experimental parameter. Typical l/s values lie between 5 and 100 dm^3/kg (10 for DEV S4). For the situation of underground disposal, it is more meaningful to use the reciprocal value, i.e. the solid-fluid ratio (s/f ratio, for DEV S4 it is 0.1), since the solid waste mass is higher than that of the leaching fluid. The s/f ratio to be expected for the post-operation water intrusion scenario can be estimated on the basis of the accessible volume in the salt mine, the amount and average density of the waste material emplaced and the density of the resulting salt solution. Values for the s/f ratio ranging from 3 to 8 kg/kg have been derived [3], which are much higher than in typical standard tests like DEV S4. Experimental constraints like possible clogging of the waste material to be leached prohibit the use of s/f ratios much higher than 0.3 to 0.5 kg/kg in single-step extraction tests. Lately a specific cascade test was developed [3] with the aim to overcome some of the general problems outlined above that are associated with the standard tests. The objective of the present work was to check the aptitude of some of the tests to predict the long term elution behaviour of toxic wastes in case of water intrusion into the salt mine.

2. METHODS

2.1. Experimental

Six mineral wastes of differing origin were selected for the experimental programme (Table 1). According to German regulation, these wastes are to be disposed of preferentially in underground facilities in former salt mines. The amount of these wastes obtained in 1993 comprises about 10 per cent of all toxic waste in Germany. The wastes with the ident numbers CA302 and CA303 stem from two different toxic waste incinerators. Full elemental analysis of the wastes was performed after complete microwave digestion using a mixture of aqua regia, hydrofluoric acid and hydrogen peroxide. For comparison the elemental composition was measured directly in ground material by powder x-ray fluorescence without further sample treatment.

Table 1
Types of waste selected for the experimental programme

ident number	waste type	amount 1993 in Germany*
CA301	reaction product from flue gas purification in toxic waste incinerators	946 t
CA302	fly ash from toxic waste incinerators	6383 t
CA303	fly ash from toxic waste incinerators	6383 t
CA304	reaction product from flue gas purification	53924 t
CA305	sludge from industrial waste water treatment	589996 t
CA306	gypsum sludge with toxic impurities	188804 t

* numbers taken from latest official statistical review of waste obtained in Germany [4]

The extraction tests were carried at room temperature following the German standard test procedure DEV S4. Several parameters of this standard test with potential impact on the mobilisation of heavy metals were systematically varied, i.e. the reaction time, the s/f ratio, the gas atmosphere, the particle size. In general 100 g waste material were dispersed in capped plastic bottles in 1000 ml solution. In order to leach the waste with high solution volumes, i.e. to realise very low s/f ratios, serial batch tests were performed, in which the waste was repeatedly extracted by new eluent for 24 h. In all extraction tests, the sample containers were rotated at about 3 rpm head-over head at room temperature, in order to reduce excessive abrasion. In addition, column elution tests, in which the eluent was recirculated, were carried out for 60 days at a s/f ratio of 0.2.

The cascade test [3] is a multistep extraction test, in which always the eluate is added to fresh waste material. Thus, with growing number of cascade steps, the s/f ratio increases. In each cascade equilibrium is reached with respect to the major ions in solution. A small sample of the eluate was withdrawn for chemical analysis, the deposits were also analyzed. The remaining eluate was weighed and the amount of waste was adapted in order to keep the s/f ratio per cascade step constant. The s/f ratio and the extraction time necessary to establish equilibrium were individually determined for each waste. Typically, a s/f ratio of 0.33 was used. The number of experimentally accessible cascade steps was between 10 and 20, resulting in a total s/f ratio in the order of 3 to 6. The number of steps is determined by the water loss in each cascade due to the formation of water-containing minerals and due to water trapping in the filter cake.

All leaching tests were performed using as eluent distilled water, a natural ground water and two different brines which are formed upon water intrusion into former salt mines. These brines are the IP9 brine, a NaCl-rich solution which is saturated in the salt minerals halite, anhydrite, polyhalite, syngenite and glauberite, and the IP21 brine, a $MgCl_2$-rich solution saturated in the salt minerals halite, carnallite, sylvite, kainite and polyhalite. The eluates were stabilized after elution by adding 1% of 1M nitric acid. The solutions were then routinely analysed by ICP-OES and ICP-MS. Chloride concentrations were determined potentiometrically. Mineral species in the original waste and in the deposit of elution tests were identified using x-ray diffraction.

2.2. Modelling

Geochemical reaction path modeling was performed using the programme system EQ3/6 [5,6]. Since the ionic strength in the eluates exceeded generally 0,5 mol/kg solution, the Pitzer-formalism [7] for calculating the activity coefficients of solute species was employed. The data base for the oceanic salt mineral system derived by Harvie, Møller and Weare [8] was used. The data base was extended with Pitzer ion interaction parameters for species containing zinc, cadmium and lead and solubility constants for respective minerals [3].

3. RESULTS

The elemental composition of the waste was determined by chemical analysis after full digestion, which provides accurate values but is time-consuming, and by x-ray fluorescence analysis, which is fast but probably less accurate. With very few exceptions, a good agreement between both values was observed for all elements. Especially in the concentration range above 500 ppm both analytical values differed typically by less than 30 per cent. Somewhat higher differences were observed in the concentration range below 500 ppm. It is concluded that for practical purposes the fast and inexpensive x-ray fluorescence technique suffices to obtain an indication of the toxic potential of the waste material.

In the DEV S4 standard test several experimental parameters were varied in order to investigate their influence on the leaching behaviour. The eluent used exerts a profound influence on the eluate pH value (Fig. 1). This also affects the leachability of heavy metals. With IP21 brine the eluate pH values are all slightly acidic to neutral and with IP9 always slightly more alkaline, even in case of waste material that reacts strongly basic with distilled water. This behaviour is attributed to the buffering capacity of the Mg ions in the brines.

Using distilled water as eluent the total leachability, i.e. the relative amount of initial waste material which is dissolved, is very different for the six wastes. At a s/f ratio of 0.05 kg/kg the following values have been determined: 0.76 for CA301, 0.36 for CA302, 0.005 for CA303, 0.30 for CA304, 0.04 for CA305 and 0.06 for CA306. These values decrease somewhat with increasing s/f ratio. Remarkable is the big difference in leachability for the two wastes CA302 and CA303 which belong to the same waste type.

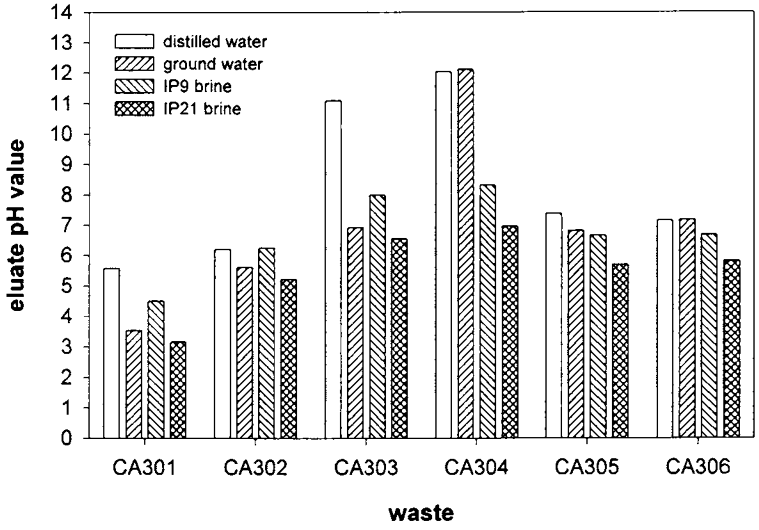

Figure 1. Final eluate pH values in single step extraction tests according to DEV S4 of the six wastes investigated for various eluents

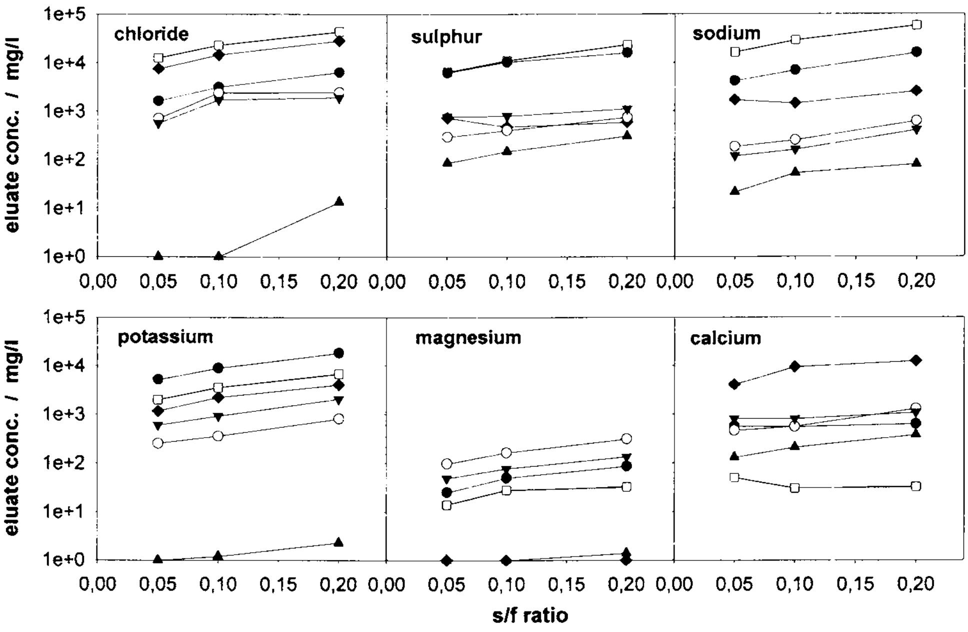

Figure 2. Leaching of the six elements of the oceanic salt system in DEV S4 tests with H_2O (□=CA301, ●=CA302, ▲=CA303, ◆=CA304, ○=CA305, ▼=CA306)

Those elements that make up the oceanic salt system are mainly responsible for the leachability (Fig. 2). Their eluate concentrations increase normally with the s/f ratio. It is observed that the total leachability is enhanced when the waste contains similar total concentrations of these cations and anions on a molar basis. For CA301 and CA304 an interrelation is observed between calcium and sulphate concentrations. An increase in sulphate concentration is accompanied by a decrease in calcium concentration and vice versa. This indicates a solution concentration control by weakly soluble calcium sulphate containing minerals.

Extraction with IP21 brine results in similar final eluate pH values for all wastes investigated. Even then differences in the leachability of orders of magnitude are observed for elements that are considered to be very soluble, e.g. zinc (Fig. 3). In general, the leaching power of the four eluents is IP21 brine ≈ IP9 brine >> ground water ≈ distilled water. A notable exception is manganese where this order is reversed.

While the s/f ratio is an important parameter, in the present examination the extraction time did not have a significant influence on the eluate concentrations, presumably because the waste materials were fairly homogeneous with a small distribution of particle sizes in the range below 5 mm. The effect of the particle size on the leachability of heavy metals was found to be small with maximum differences of 50 per cent between highest and lowest solution concentrations. Extraction under an inert gas atmosphere also had only a slight influence on the leachate concentrations without any unequivocal trend. Hardly any differences were observed even for elements like iron, chromium and manganese that can exist in different oxidation states. This finding is attributed to the waste material being fully oxidised prior to the extraction experiment owing to its contact with atmospheric oxygen.

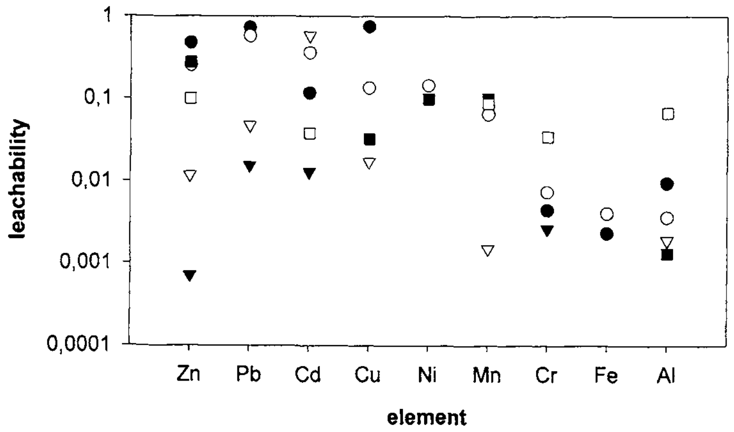

Figure 3. Leachability of some metals by IP21 brine at a s/f ratio of 0,05 kg/kg (•=CA301, ○=CA302, ▼=CA303, □=CA304, ■=CA305, □=CA306).

With increasing s/f ratio the absolute heavy metal concentrations in the eluates increase in most cases. Figs. 4 and 5 display the combined results of various leaching tests with wastes CA301 and CA304, respectively, using IP21 brine as eluent. The solid lines represent the total amount of the elements in the waste. The distance between individual data points and the solid lines at any given s/f ratio indicates the leachability of that element. Obviously, the leaching behaviour of the two waste materials is very different. For CA301 leachability decreases only slightly with increasing s/f ratio, while a steep decline is apparent for CA304 which indicates some kind of solubility control.

The results of DEV S4 tests and serial batch tests correspond well with each other, while the results of column elution tests deviate sometimes significantly. Higher eluate concentrations in the column elution test, e.g. Zn in Fig. 5, indicate that other slow release mechanisms are operative which are not effective during the short time tests. Lower eluate concentrations in the column test suggest that these elements are slowly removed from solution via precipitation of respective saturated mineral phases or via coprecipitation. Both cases are relevant for the leaching behaviour of the waste at underground disposal conditions. In any case, from these results it is very difficult to extrapolate to representative s/f ratios. The results for the other waste materials studied lie in between the two extremes shown.

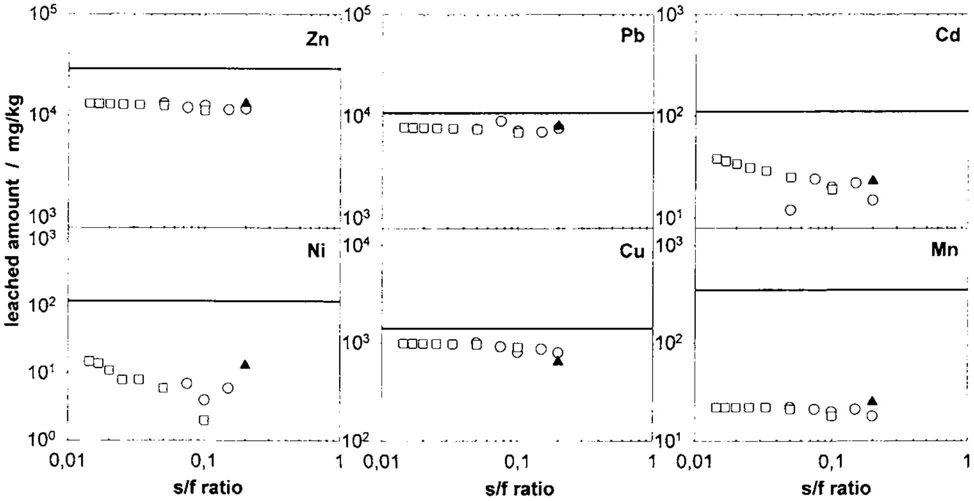

Figure 4. Dependence of the leached amounts of some elements on the s/f ratio for various leaching tests with waste CA301 and IP21 brine. (○ = DEV S4, □ = serial batch test, ▲ = column test)

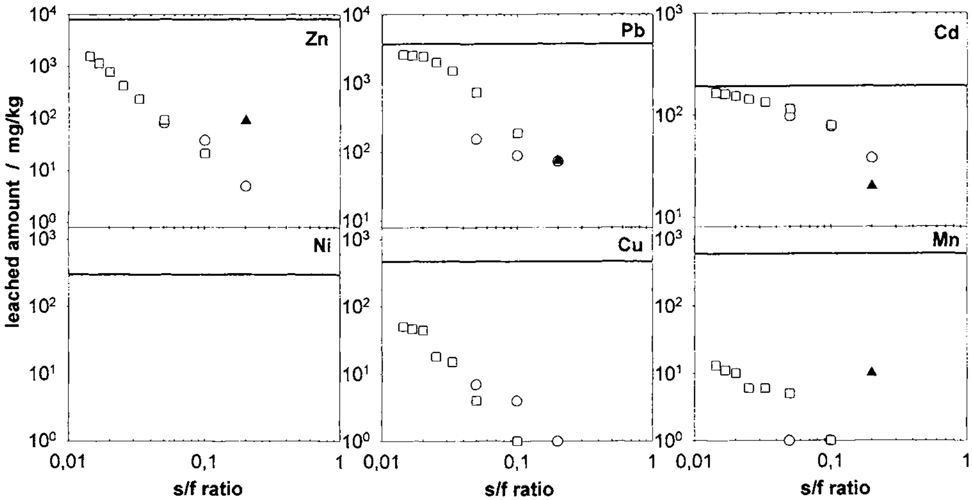

Figure 5. Dependence of the leached amounts of some elements on the s/f ratio for various leaching tests with waste CA304 and IP21 brine. (○ = DEV S4, □ = serial batch test, ▲ = column test)

The experimental results of the cascade test with waste CA302 and distilled water as initial eluent are shown in Fig. 6 (symbols). An s/f ratio of 0.33 was used per cascade, so a total s/f ratio of 5 was reached at the last cascade. This value is well within the range which is to be expected for a post-operation water intrusion into an underground disposal facility in a former salt mine in Germany. With increasing s/f ratio during the test, the major ions reach high concentrations of several mol/kg H_2O, so the final solution is a concentrated brine.

The lines in Fig. 6 represent the results of geochemical modelling calculations. Only the species shown could be modelled owing to the existing database. Therefore, the 'model waste' was composed of only these species in their real ratio but corrected for their individual leaching rates, which were derived from the results of DEV S4 tests using a low s/f ratio. Finally, the charge imbalance between cationic and anionic species was accounted for by small corrections in the species concentrations. The mass of the elements not considered was taken into account by a proportionality factor applied to the reaction progress variable. A good correlation between measured and calculated solution concentrations is obtained, even the sharp peak in the Ca concentration in the first cascade is correctly predicted. The deviation in the measured Mg concentrations, on the other hand, can not be explained, since the solution concentration increase from the 13th to the 14th cascade is higher than the amount of Mg introduced in one cascade by new waste material. Therefore, we tend to attribute this behaviour to an analytical artefact in the 7th to 13th cascade.

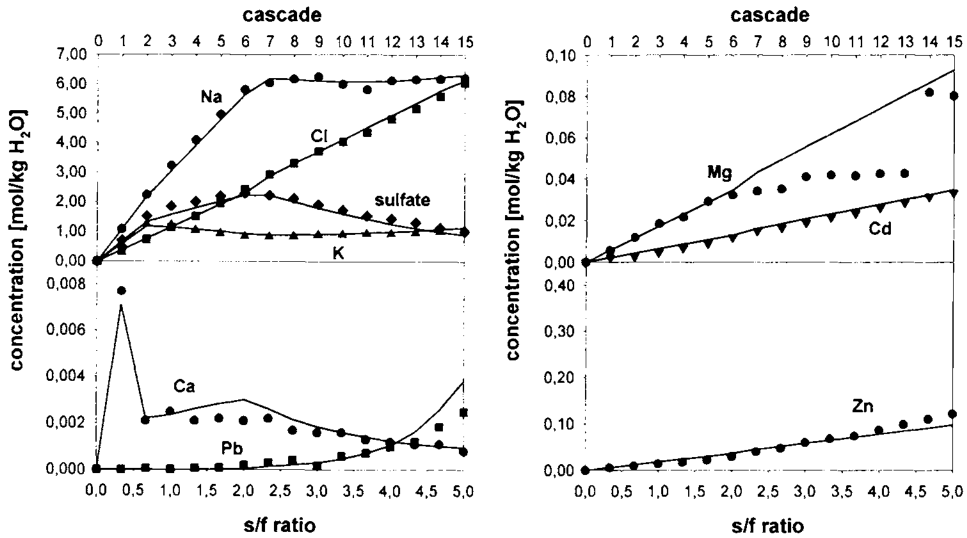

Figure 6. Experimental data (symbols) and modelling results (lines) for solution concentrations in the cascade test of CA302 and distilled water as initial eluent

Independent corroboration for the quality of the geochemical modelling is derived from a comparison of the minerals that have been identified in the deposit of each cascade by x-ray diffraction and the minerals that are precipitated according to the geochemical modelling (Table 2). Again, a very good correlation has been found. The small halite signals in the first 11 cascades are most likely due to water evaporation from minute leachate droplets which remained on the solid sample after separation of the liquid phase. Glauberite, on the other hand, can only be detected by x-ray diffraction at a weight mass of above 3 %, i.e. at much higher concentrations than are predicted by geochemical calculations to be precipitated in these experiments.

The geochemical modelling provides insight into the reaction pathway. Certain striking features of the data curves can be attributed to specific reactions and processes. Such a complete understanding of a system allows one also to study the influence of some of the boundary conditions on the results, rendering time consuming experiments unneccessary. For example, at s/f ratios above 5.5 the lead concentration will level off at a value slightly above 0.004 mol/kg H_2O, since solubility limits of sulphate containing lead minerals are reached. In case of IP21 brine as eluent, these solubility limits are reached already at lower s/f ratios. From the experimental results of the single-step leaching tests alone, it would have been impossible to predict such a behaviour.

Table 2
Comparison of minerals identified in the deposit by x-ray diffraction (x) and calculated precipitates (●) for the cascade test of waste CA302 and distilled water (symbols in brackets represent weak x-ray signals)

cascade	halite	syngenite	aphthitalite	glauberite	thenardite
1	(x)	x - ●			
2	(x)	x - ●	●		
3	(x)	x - ●	x - ●		
5	(x)	x - ●	x - ●		
7	(x)		x - ●	●	x - ●
9	(x)		x - ●	●	x - ●
11	(x)		x - ●	●	x - ●
13	x - ●	(x)	x - ●	●	x - ●
15	x - ●	(x)	x - ●	●	●

Similar correlations between experimental data and results of geochemical calculations have been obtained for other cascade tests using IP21 brine as eluent and/or different wastes. It is concluded from these results, that geochemical modelling can be a suitable tool to predict the leaching behaviour of waste material in contact with solutions of different salinity up to high s/f ratios. Apart from a suitable data base for the geochemical modelling, data on the chemical composition of the waste and the individual elemental leaching rates are prerequisites for a successful calculation.

Fig. 7 shows the results of geochemical equilibrium calculations for DEV S4 tests which have been carried out with waste CA301 at various s/f ratios. In contrast to the results of the cascade test, the theoretical results show a poor correlation for sulphate, sodium and potassium concentrations. Especially, the calculated sulphate concentrations are systematically lower than the measured ones. This effect is more pronounced at higher s/f ratios. Taking into account that sulphate minerals are known to precipitate slowly from saturated solutions, this effect indicates sulphate oversaturation which is not equilibrated during the short time frame of the DEV S4 test. If mineral precipitation is suppressed in the geochemical calculations for all sulphate minerals but anhydrite, a much better correlation is obtained (Fig. 8). The precipitation of anhydrite has to be allowed in order to control the calcium concentration. This modelling approach is rather arbitrary, since nothing is known about the actual degree of sulphate mineral precipitation. However, the results clearly support the conclusion regarding sulphate oversaturation in DEV S4 tests which may affect not only the solution concentrations of the other major elements but also of the heavy metals.

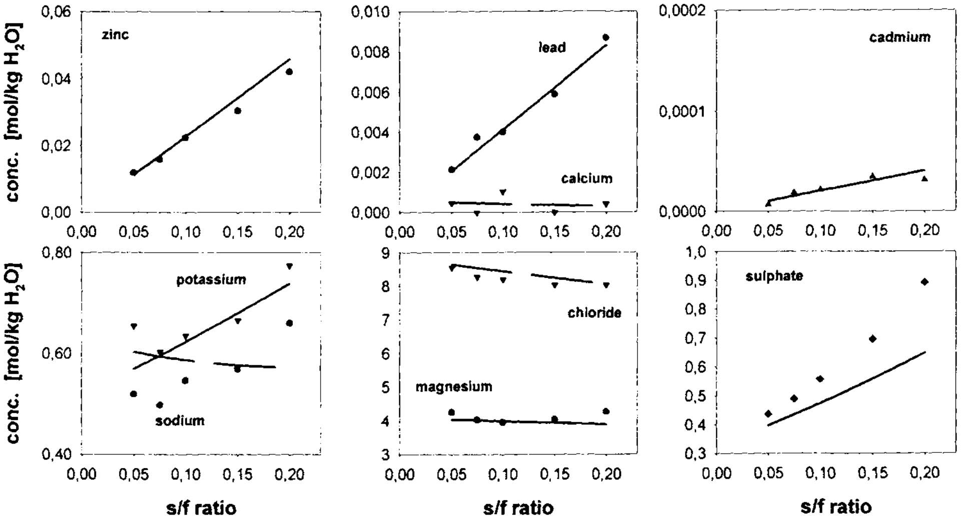

Figure 7. Experimental data (symbols) and modelling results (lines) for solution concentrations in DEV S4 tests of waste CA302 using IP21 brine as eluent.

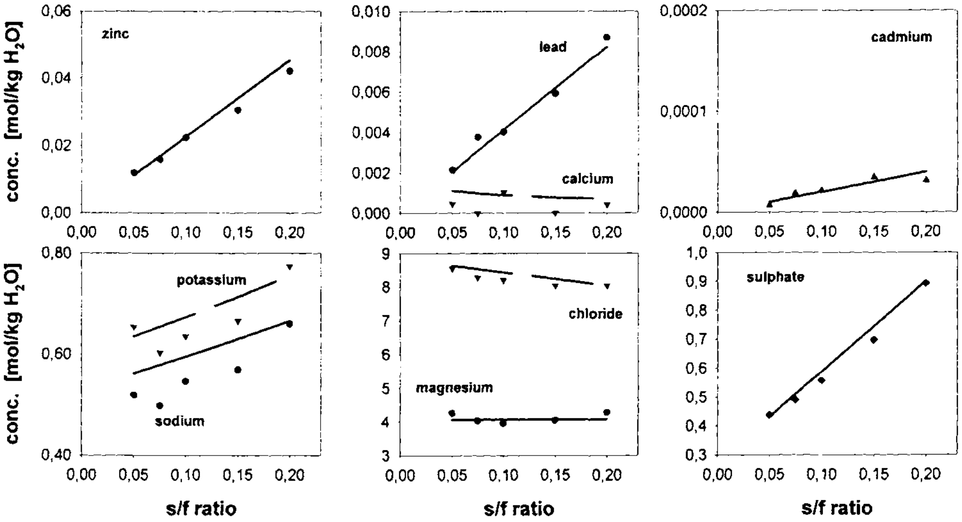

Figure 8. Experimental data (symbols) and modelling results (lines) for solution concentrations in DEV S4 tests of waste CA302 using IP21 brine as eluent with supressed sulphate mineral precipitation except anhydrite.

4. DISCUSSION

It is shown that single step extraction tests with distilled water or low ionic strength ground water can be misleading with respect to the mobilization of heavy metals by high saline solutions, since the latter have a higher leaching power and buffer the eluate pH to some extent. Furthermore, it is difficult – if not impossible – to extrapolate the experimental results from the s/f ratios used in single extraction tests or in column tests to the required high values.

Most insight into the reaction pathway is gained by the cascade test where the leachate of each cascade is added to new waste material. In this way s/f ratios of 3 to 8 (kg/kg) can be reached which are representative of underground disposal facilities upon water intrusion. Such high s/f ratios are normally inaccessible by single elution tests or column elution tests. The cascade test, therefore, is a means to arrive at a realistic estimate of the source term for heavy metal elution from mineral wastes. However, the expenditure renders this test unacceptable as compliance test for practical everyday application by waste producers.

Our results suggest that model calculation may bridge the gap since good agreement was observed with experimental data from cascade tests. However, at present the data base required for geochemical model calculations for high saline solutions is still limited and has to be completed.

Indispensable parameters for model calculations are content and leaching rate of the waste ingredients. The content can be determined with sufficient accuracy for this purpose via powder x-ray fluorescence. The leaching rate can be determined in many cases by single day extraction tests such as the DEV S4, adapted to the respective eluent and a suitable, low s/f ratio.

Model calculations also showed that non-equilibrium situations may prevail in short-time tests such as DEV S4. Several sulphate minerals, that are saturated in solution, do not precipitate within the time frame of the leaching experiment. Therefore, we suggest that the validity of model calculations based on input parameters derived in single day experiments be checked against experimental data from elution tests where equilibrium has been attained.

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Waste Materials in Construction
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Disposal options for Spent Potlining

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Steel-shelled electrolytic pots are used by the aluminium industry to produce the pure metal from aluminium oxide. The pots contain two linings, one typically consisting of block insulation to reduce heat losses, and a second consisting primarily of anthracite and pitch. The second liner serves as the cathode of the electrolytic cell.

An electrolytic cell is operated until the double lining fails, typically a three-to-ten year period. During the operation of the cell, fluorides, aluminium, cyanides and PAH's are absorbed into the cell lining.

Spent Potliner (SPL) was listed by EPA in 1988 as a hazardous waste, mainly because it contains significant amounts of iron cyanide complexes and free cyanides. The need for an economical and environmental acceptable means for SPL disposal, led the Norwegian aluminium industry, which produces annually 25 000 tons, to support a number of research projects aimed at finding a sustainable use of SPL.

This paper discusses 3 important subjects of SPL disposal: leaching characteristics, challenges in chemical analysis and the possibilities of utilisation of SPL in the cement industry.

Keywords: Spent Potlining, Leaching, Chemical analysis, Utilisation, Cement Industry.

1. INTRODUCTION

Spent potliner composition can vary significantly from site to site. The range of analyses is given in Table 1 [1]. The foremost constituents are fluoride, aluminium, sodium and carbon. Although only a trace constituent, cyanide is at the centre of the regulatory controversy regarding SPL. The cyanide, present in varying concentrations from 0.002 to 0.6%, is formed during the smelting process from the reaction of atmospheric nitrogen with the carbon pot liner [2]. Fluorides are also of regulatory concern [2]. Spent potliner contains a high level of fluoride, ranging from 7 to 22%. Fluoride and fluor complexes are highly water-soluble and leach out easily from SPL disposal sites. They can therefor cause adverse effects on groundwater and fresh water receiving streams if discharged without treatment. Eluates may have health effects on humans, plants and animals.

The EPA has listed SPL as hazard waste because of: (1) SPL contains iron cyanide complexes in significant concentrations; (2) both free and iron cyanides are toxic; (3) free and iron cyanides are leachable, especially from unprotected disposal sites and under conditions of acidic precipitation; (4) iron cyanides are photoreactive and may result in the release of hydrogen cyanide; (5) improper disposal of SPL has been demonstrated to result in a substantial hazard to the environment due to the migration, mobility and persistence of cyanides; and (6) SPL is generated in large quantities.

Table 1
Range of composition of spent potlining (%)

	Cathode carbon	Refractory
C	54-60	2
Na	12-16	0.7-15
Al	7-10	16-19
F	10-14	16-20
Ca	0.7-1,3	1-2
Si	1.3-2	7-10
Fe	~2	~3
CN	0.2-0.3	0.1-0.3

The aluminium industry has long recognised the environmental challenges of SPL and is pursuing many options for treatment and/or disposal. These options include: Landfilling, recycle as a feedstock in other industries (such as the steel, aluminium or mineral wool industries); fluidized bed combustion; cryolite recovery; pyrohydrolysis, pyrosulfolysis and other. Landfilling is an option that is presently available but will become increasingly expensive since hazardous waste landfills are required. Recycling through other industries is an attractive option; however, the classification of SPL as a hazardous waste greatly discourages other industries from utilising SPL due to the cumbersome and expensive environmental regulations. Some of the other techniques may eventually have application, but many involve excessive cost and have never been proven on an industrial scale.

1.1. Leaching characteristics

Over the years much of the SPL in Norway was placed in landfills or used for landscaping. However, the volume of SPL generated, and its chemically composition, create potentially serious environmental and logistical concerns for the industry, as SPL is listed as a hazardous waste, according to European and US regulation.

This means that this waste is subject to regulations that require that the waste are characterised and that it meet specified criteria, if permission for utilisation is to be granted. The characterisation required have often been based on the performance of specific leaching tests, and the criteria to be met are usually specified in terms of associated limit values for the concentrations (e.g. mg/l) or various components in the eluate produced or the amounts (e.g. mg/kg of waste product tested) of various components leached.

In this paper we discuss the leaching behaviour of SPL waste based on batch, column and lysimeter tests.

1.2. Chemical analysis

SPL has a high content of especially sodium and fluoride. These high concentrations induce a series of analytical challenges, which must be solved. In the determination of trace elements, different analytical techniques should be considered, but in most cases multi-element techniques such as ICP-AES or ICP-MS are preferred because of the much higher sample throughput. For the ICP-MS the high sodium content leads to a high content of dissolved solids, and depending on which instrument is used, the samples need to be diluted before the trace and major element determination. In our case ICP-AES is used for the element determinations, and high contents of alkali will contribute to a significant change in the plasma conditions. To correct for this, both dilutions and the use of internal standards are necessary. Still, a systematic error originating from the change in plasma conditions induced by the content of alkali, is present, and even though it is minimised by dilution and the use of internal standards, it is in the order of 20% for some trace elements. Without the use of ionisation buffers this will be difficult to correct for, since the alkali content in the samples is not constant.

Another problem present during the analysis of SPL is the relatively high content of cyanides. Before analysing with ICP-AES, acidifying with an acid (i.e. nitric acid) is necessary, with the generation of HCN (g) as a result. This gas is highly toxic and special measures should be taken to protect the personnel handling the samples.

The presence of cyanides and fluorides is also an analytical challenge, as they are relatively strong complexing agents for some elements. To speciate the metals are therefore an important task before any conclusions are drawn from the analysis regarding environmental hazards and risks. To speciate the metals using only computer modelling programs is not preferred, even if this modelling is a necessary step in the understanding of the chemistry of interactions. Most modelling programs are not capable to model the complexing chemistry with the accuracy needed at the ionic strengths present in percolates originating from SPL. And even if they are, it has to be verified. Hence, analytical techniques for speciation are needed. Many of these techniques described in the literature are very time-consuming and expensive. Given that it is sufficient to measure the overall complexing capability of the SPL-solutions, some simplifications may be done to reduce the analytical costs.

1.3. Utilisation of SPL in the cement industry

The potential for utilisation of SPL in the cement industry is investigated. The most obvious benefit would be to replace some of the fossil fuel and the aluminium source used in cement production. However, the high content of sodium and fluoride in SPL constitute a potential problem in the preheater/precalciner cement processes in Norway. In addition, problems associated with handling, i.e. crushing and high concentration of cyanides, have to be solved. All benefits and drawbacks will be accounted for in the oral presentation.

2. EVALUATION OF THE POSSIBILITIES OF UTILISATION OF SPL IN THE CEMENT INDUSTRY

In brief, Portland cement is made as follows: an argillaceous material (clay) and a calcareous material (limestone) are crushed, mixed and ground to a fine powder. The total composition of this mixture must be kept constant within narrow limits, as any wide departure from the optimum may result in inferior cement. The plant operation and the quality of the final product both put narrow limits to variation in the chemical composition of this mix. The mixture must be correctly proportioned, finely ground and thoroughly intermixed before entering the huge rotary kiln.

The mixture then passes into the rotary kiln where it moves slowly down the kiln and is heated slowly to the sintering point. The humidity and carbon dioxide from raw materials are driven off before the high temperature clinking zone is reached. As the hotter regions are approached, chemical reactions take place between the constituents of the raw mixture. In the course of these reactions new compounds are formed, and some of these melt to partially fuse of charge. The material is burned at temperatures above 1450°C to form a hard nodular "clinker" consisting of newly crystallised calcium silicates surrounded by interstitial calcium aluminate and calcium aluminoferrite compounds, with minor amounts of other reaction products.

Depending on the process type, between 800-1400 kcal/kg energy is consumed in this clinker production. Typically, a cement kiln is fired with coal, petroleum coke, oil, or natural gas. However, since the 1970s, more and more production facilities utilise different kinds of waste as well as used oil and tires to replace a portion of their conventional fuel.

After leaving the rotary kiln the clinker drops into a cooler. When cooled. the clinker is conveyed to the cement mill, where it is mixed with gypsum and this mixture is ground to a very fine powder. That powder is Portland cement of commerce. The ground cement is conveyed to silos where it is stored until tested and shipped. All cement must conform to certain standard specifications as to compositions, particle size, strength and other physical properties.

The properties of the final cement product depend on raw materials and the way they are processed. All raw materials are naturally formed and they vary widely chemically, mineralogical and physically.

In Norway, clinker is produced in modern preheater/ precalciner kilns. These kilns are equipped with a tower of heat-exchanging cyclones (i.e., a preheater) in which the dry feed is preheated and partially calcined by the kiln's hot exit gases prior to entering the precalciner and finally the actual kiln. The precalciner is a secondary firing device and is added to the lower stage of the preheater in which further calcination of the material occurs. Consequently, the majority of the material that enters the kiln is completely calcined. Because of the build-up of volatile components such as alkali salts in the lower stages of the tower and kiln entrance, the preheater kiln is often equipped with a bypass to divert a portion of the kiln's hot exit gases from the tower to the air pollution control devices.

The cement kilns are fired with coal and petroleum coke. The coal is ground or pulverised by on-site equipment adjacent to the kiln and is pneumatically injected into the back end of the kiln and into the precalciner. The back end of the kiln is the end at which products are discharged.

Two options have been considered for the re-use of SPL in the Norwegian cement industry: either the carbon fraction can be used for its fuel value, or the refractory fraction can be used as a raw material substitute, i.e. alumina and silica.

In both cases, one has to carefully consider the sodium and the fluoride balances of the cement kiln where SPL may be recycled. Those two elements are commonly present in the raw materials coming from the clay and limestone quarries. The proportion of SPL accepted by the process will depend mainly on the proportions of sodium and fluoride already present in the process, since there is a limit for both of them in the process and in the final cement.

Taking into account the pre-existing levels of alkaline compounds in the raw materials, it was found that the addition of carbon SPL above 0.5% would be complicated. The carbon SPL contained 73% fixed carbon with a burning value of 6055 Kcal/kg and an ash content of 26%. The volatility was measured to be 0.9 % and the burnabillity was regarded as low. The carbon SPL also contained 16.3% fluorine and 12.6% sodium, which could cause alkaline build up and possible cyclone blockage. Simple leaching experiments performed in the laboratory at a liquid to solid ratio of 10 showed that it could be possible to remove around 16% and 28% of fluorine and sodium respectively. This would not be enough to prevent potential blockages in the cyclone tower or additional fluorine and sodium content in the final cement. In addition to this, the carbon SPL is a very hard material, which would be difficult to ground in the on-site coal mill.

The refractory SPL fraction, on the other hand, contains 53% SiO_2, 36% Al_2O_3, 2% Fe_2O_3, 0.6% CaO, 0.4% MgO, 1.6% K_2O, 0.3% Na_2O and 0.005% fluorine. The refractory SPL can also be ground in the primary crusher on-site together with the raw material. Based on this it is decided to carry out a full-scale experiment in the spring 2000 where around 1% of well sorted refractory SPL is fed to the raw material line of a Norwegian Cement Plant.

3. LEACHING TESTS

In order to provide adequate tools for assessing the environmental impact of SPL disposal sites and large-scale land application of SPL, reliable methods for predicting the leaching and emission of potential pollutants from landfilled and/or in marine environment, SPL must be verified. The amount of detailed information available on the quality of percolate from existing SPL landfills is very limited and totally insufficient for predictive purposes. In particular few, if any, field data exist that describe the variation of quality with time. The lack of data is easily explained by the difficulties involved in the close monitoring of full-scale SPL disposal site: the system is often ill-defined, and it may be difficult to obtain a reliable water balance for the site and, in turn, to relate the water balance data to the observed eluate quality. It may also be difficult to distinguish between true percolate and percolate diluted with groundwater. For older sites, historical data on the quantity and quality of deposited SPL disposal site are not always available.

Predictions of the quality of percolate and its variation with time at planned or existing SPL landfills sites must therefore be based on the results of smaller-scale leaching tests with typical SPL. The most accurate predictive estimates of the leaching behaviour of landfilled SPL can probably be obtained from lysimeter tests and accelerated laboratory leaching tests. These tests simulate to a greater or lesser degree the leaching conditions at an actual landfilled site.

The information on leaching behaviour obtained from lysimeter and column tests is much more detailed than that obtained from batch tests, and the variations in percolate/ eluate composition during the initial leaching period can be studied only by lysimeter and column leaching techniques. Long-term leaching behaviour is often simulated more conveniently by multiple batch-leaching tests.

In this project we have studied the mobility of different compounds, as CN^-, F^-, heavy metals and PAH for marine- and land-lysimeters and compared with different short and long term laboratory leaching experiments, which included the new European draft standard percolation test for basic characterisation.

All the test results are not available yet, but will be presented in the oral presentation.

3.1. Experimental

3.1.1. The cathode cell investigated in this study

A used cathode from Sør-Norge Aluminium A/S was chosen to represent a typical cathode in the Norwegian aluminium industry. This cell represents the prebake technology and had been operated for 1635 days before dismantling. The cell weighed 35100 kg, and was 8 m long, 3,5 m wide and 1,5 m high.

The hearth or lining of the cell is composed of carbon, which is backed by insulation and contained within a steel container called a pot shell. The carbon portion of the lining serves as the cathode and contains the molten electrolyte. The carbon lining is composed of prefabricated carbon blocks joined together by a carbon paste, which is hydraulically rammed, in the seams between the carbon blocks. The sidewalls of the lining are formed with carbon paste and SiC blocks. The carbon material within the lining, both blocks and paste, is predominantly anthracite-based material. They contain some graphite to improve their electrical and thermal properties. Insulation packages for a cell are refractory bricks; first layers of Chamotte stones, followed by layers of Moler stones and in the bottom of the cell, a layer of calciumsilicate.

3.1.2. Dismantling of the cathode

The used cathode was emptied at a special site in the open air. Using an excavator, the cell was dug out in the dry state. The cell was allowed to cool down before breaking up the dry mass. During the dismantling process, the slab aluminium and frozen bath are salvaged and recycled into the process. In this project we divided the cell material in two equal halves. The one half was crushed and homogenised and should be representative for the "total cell". The other half was separated into three different cuts:

1st Cut	The carbon liner
2nd Cut	The part of the refractory material that was close to the carbon lining (Chamotte stone)
3rd Cut	The part of the refractory expected to be least contaminated (Moler stone).

3.1.3. Sample preparation

The different part of the cells was crushed on site using a jaw crusher. Afterward the fractions were homogenised mechanically, using suitable equipment, before transported to SINTEF in big bags of approximately150 kg. At SINTEF samples of 10 kg were chosen randomly and crushed with a hammer to a fraction <4 mm. This fraction was further homogenised by trombling for 48 hours. A sub-fraction of this was further ground to <125 µm. Different fractions of SPL were subjected to chemical analysis.

Figure 1. The dismantling of the cathode. The right half was crushed down and homogenised and should be representative for the "total cell". The left half was separated into three different cuts as visualised in Figure 2.

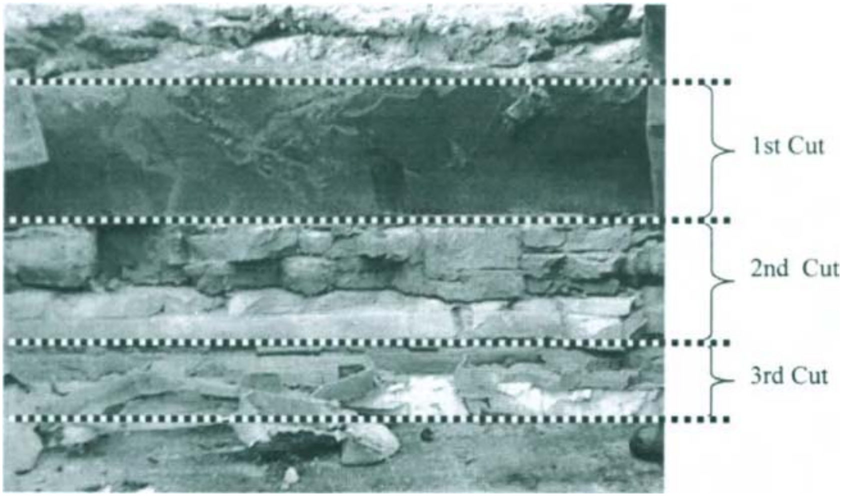

Figure 2. The left half of the cathode (in Figure 1) was separated into three different cuts: the carbon liner (1st cut), the Chamotte stone (2nd Cut) and the Moler stone (3rd Cut).

3.1.4. Sampling for the tank-test

A well-defined geometric shape of different part of the cathode cell was sawed out from the 1st, 2nd and 3rd Cut using a special diamond saw blade. This task was very hard and time-consuming due to the fact that we could not use cooling-water in the saw operation. For the tank-tests we also included a 4th Cut, consisting of bottom-blocks of calcium silicate.

3.1.5. Laboratory leaching tests on SPL

3.1.5.1. Granular SPL

Samples of granular (< 4 mm) SPL were subjected to column and batch leaching tests with artificial ocean water and artificial rain (demineralized water acidified to pH 4 with HNO_3), according to NEN 7343, NEN 7349 and CEN/TC 292 [3,4,5].

In the column test [3] approximately 0.6 kg samples of the SPL fractions ("total SPL", 1st Cut, 2nd Cut and 3rd Cut) were placed in plexi-glass columns of 5 cm in diameter and 20 cm high. The samples were leached with seawater and artificial rain respectively, in up-flow at a flow rate corresponding to 0,015 l/hour. Eluate fractions corresponding to the liquid/solid ratios (L/S) = 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 l/kg were collected from each of the columns and subjected to chemical analysis.

Samples of fractions of SPL were subjected to two different batch leaching tests: 1) the CEN/TC 292 two steps compliance test for granular waste at liquid/solid ratios (L/S) = 2 and 8 with demineralized water and seawater [5]; 2) a sequential batch leaching with acidified water (pH = 4) and seawater at L/S = 20, 40, 60, 80 and 100 l/kg according to NEN 7349 [4]. The fractions were filtered through a 0.45 μm filter and analysed.

Samples of ground (< 125 μm) SPL were also subjected to availability test, NEN 7341 [6], in order to determine the maximum leachability.

The collected eluate fractions were analysed for pH, conductivity, fluoride, total and free cyanide, Na, K, Ca, Mg, Al and heavy metals. Some of the collected eluates were also analysed for PAH.

3.1.5.2. Tank leaching test

Pieces of the different fractions of the SPL were subjected to dynamic tank leaching, NEN 7345 [7], with artificial rainwater and seawater in order to determine the rate of release of key contaminants from cube shaped specimens. In the tank leaching experiments, each of the monolithic waste forms was suspended in a closed waterfilled polypropylene tank by a nylon string. At certain intervals (increments of 0.25, 1, 2, 5, 9, 16, 36 and 64 days) the water was replaced with new eluate and analysed for pH, conductivity, fluoride, total and free cyanide, Na, K, Ca, Mg, Al and heavy metals, after filtration through a 0.45 μm filter. This allows the calculation of the flux of the elements (mg/m^2) as a function of time.

3.1.6. Lysimeter tests

3.1.6.1. Land lysimeter

At Hydro Aluminium, Karmøy, a lysimeter test was carried out on the following materials:

1) The "total cathode material" crushed to 4-20 cm (1000 kg)
2) 1st Cut crushed to 4-20 cm (1000 kg)
3) The dust of "the total material" (200 kg)
4) "Blind lysimeter" (for collecting the rainwater)

The tests were performed in test bins of 1 m^3 made of fibreglass reinforced polyester. The lysimeters were facing the open air, and the rainwater was collected at regularly intervals for analyses of the percolate. The samples were chemically analysed for main elements, anions, trace elements and PAH. All samples were filtrated and a number of the filter–residues were subjected to further analyses, especially concerning PAH.

A station for continuous collection of meteorological data, i.e. on wind speed, temperature, humidity and precipitation is established permanently on the lysimeter field.

In the case of laboratory leaching tests, measured concentration of main elements, anions and trace elements are generally related to the liquid-solid (L/S) ratio. In order to do this for the lysimeter tests as well, the real time scale was converted into the L/S scale with the help of the liquid balances.

3.1.6.2. Marine lysimeter

In addition two test bins, each of 1 m^3, were placed in the sea at Hydro Aluminium, Karmøy.

The lysimetes were filled with the following materials:

5) The "total cathode material" crushed to 4-20 cm (1000 kg).
6) 1st Cut crushed to 4-20 cm (1000 kg).

These lysimeters were constructed in such a way that the seawater freely could wash in and out of the lysimeter cells. The purposes of this investigation were to study the washout effect of some key contaminants of the SPL.

3.1.7. Analytical methods

Solids: Analyses for major elements were done by x-ray fluorescens. Trace element analyses were performed by ICP-AES, ICP-MS and AAS after digestion of samples in Teflon bombs using a micro-wave oven and different mixtures of acids, for example HNO_3 or HCl + HNO_3 + HF.

Eluates: Metal and trace element analyses of eluate were performed using ICP-AES and AAS. Prior to the analysis, the samples were acidified to $pH < 2$ by addition of HNO_3. The generated HCN was removed by bubbling the solution with argon gas. The cyanide content has been determined by distillation of cyanide as HCN, followed by a spectrophotometric or titrimetric determination of HCN. The fluoride content was determined using a fluoride ion-sensitive electrode.

3.2. Preliminary leaching results

The test results from all the tests are not available yet. The lysimeter tests have only been in operation for six month, but they are planned to be followed until L/S =5, which will take almost ten years to achieve. In this paper we present some results obtained for 1st Cut SPL.
In Figure 3, the composition of the eluates from a column tests of 1st Cut SPL are plotted versus L/S. The major components of eluates from 1st Cut SPL are inorganic salt ions, as for instance sodium, aluminium, calcium, potassium, fluoride and cyanide. The trace elements present in some amounts are nickel, zinc and arsenic. Zinc and arsenic form oxyanions species under alkaline conditions. Over a L/S range of 0-10, the concentration of most parameters decreases with increasing L/S.

The results of the lysimeter leaching tests, the column leaching tests, the CEN test and the availability test are compared in Figure 4a-4g for a number of eluate components for 1st Cut. The plots of cumulative amounts leached versus L/S show a good general agreement between lysimeter and laboratory leaching results, particularly for fluoride and sodium.

For cyanide the availability test show that the amount released is lower than for the CEN and column test, probably due to loss of cyanide caused by the formation of HCN at pH = 4. The agreement between the CEN and column test is good. For the lysimeter test we have too few points yet to see how the curve runs. The determination of the cyanide content in the 1st Cut sample itself is not yet finished.

For aluminium, nickel, zinc and arsenic the concentration of the eluates from the column test seem to be low compared to the CEN test and the trend from the lysimeter test. We will repeat this column test to verify if this difference in leaching is real.

The pH of the eluates is shown in Figure 5. The 1st Cut SPL material is alkaline and controls the pH. The alkaline nature of the SPL is probably dictated by its content of F and CaO and result in a pH range from 10-13.

Releases of some majors and trace elements in the tank leaching test of 1st Cut SPL is shown in Figure 6. The major components of eluates are inorganic salt ions, as sodium, aluminium, calcium, potassium, iron and sulphate. Typical trace element present in some amounts is nickel.

3.3.Conclusion

This project has only been running for ¾ years, and will be continued next year. The amount of data at this stage is thus too limited to be used for a major conclusion.

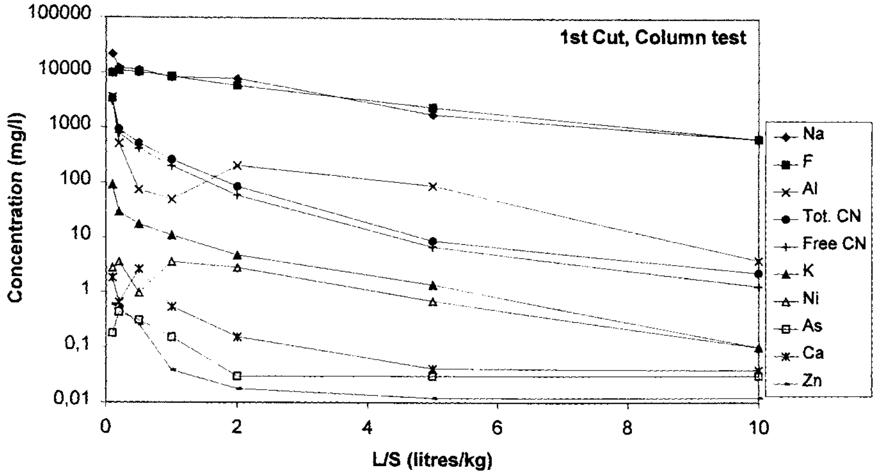

Figure 3. Some major and trace elements in eluate from column test.

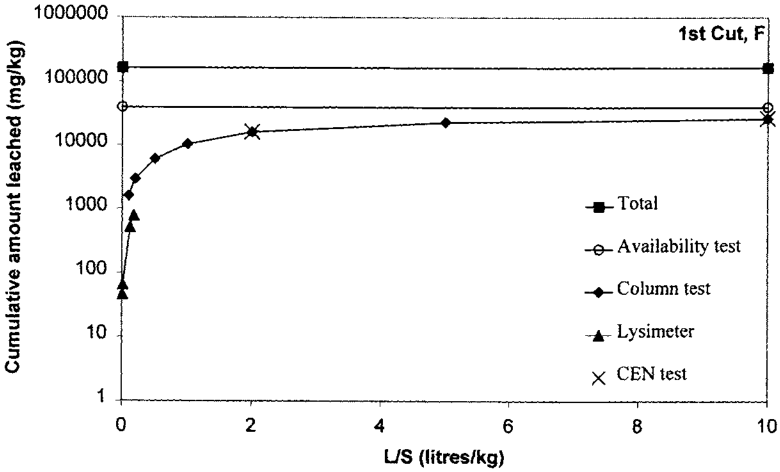

Figure 4a. Comparison of column-, CEN-, availability and lysimeter test. The cumulative leaching of F^- as a function of L/S.

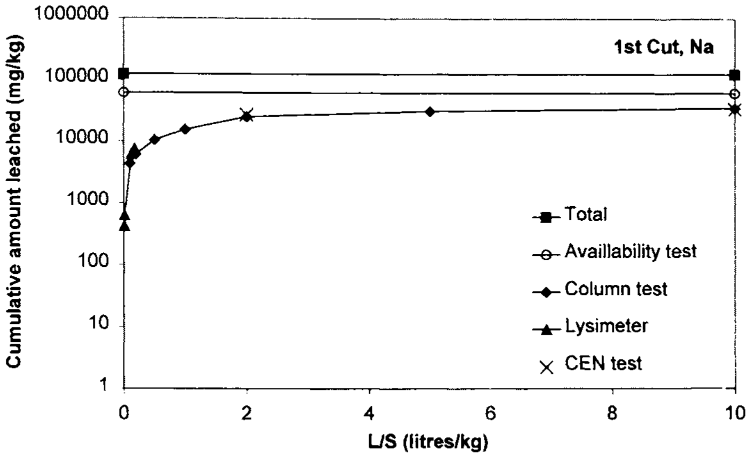

Figure 4b. Comparison of column-, CEN-, availability and lysimeter test. The cumulative leaching of Na as a function of L/S.

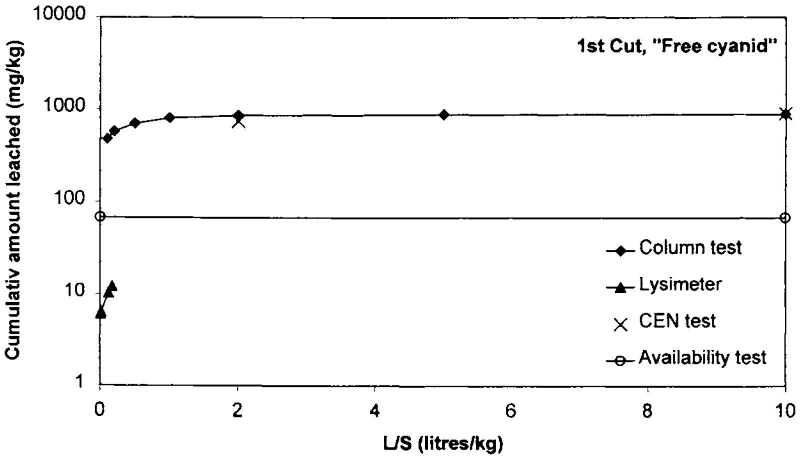

Figure 4c. Comparison of column-, CEN-, availability and lysimeter test for major and trace elements for 1st Cut, SPL waste. The cumulative leaching of cyanide as a function of L/S.

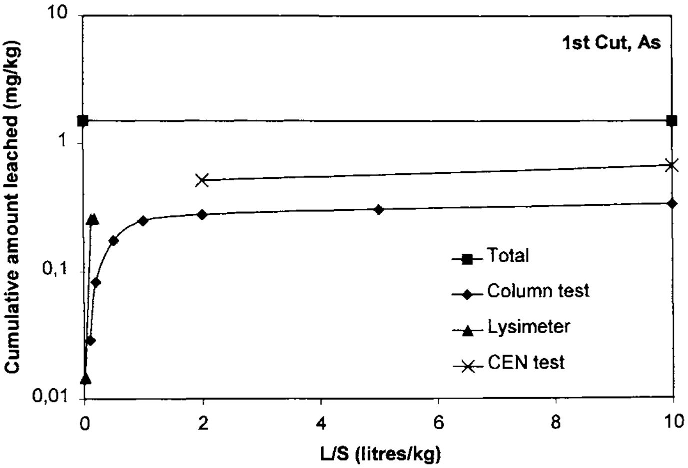

Figure 4d. Comparison of column-, CEN and lysimeter test. The cumulative leaching of As as a function of L/S.

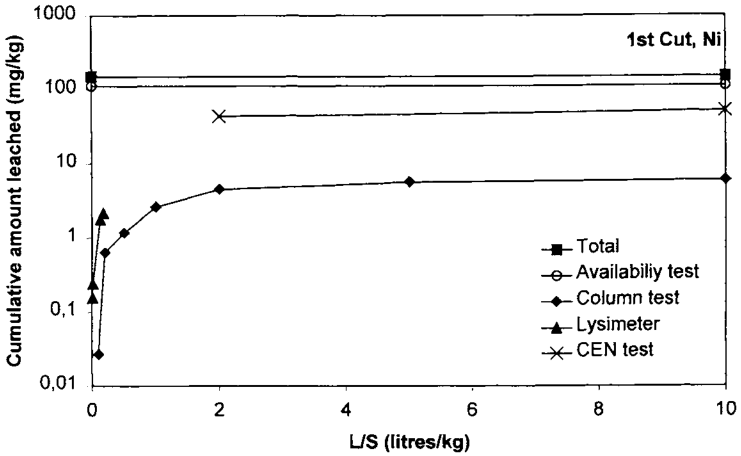

Figure 4e. Comparison of column-, CEN-, availability and lysimeter test. The cumulative leaching of Ni as a function of L/S.

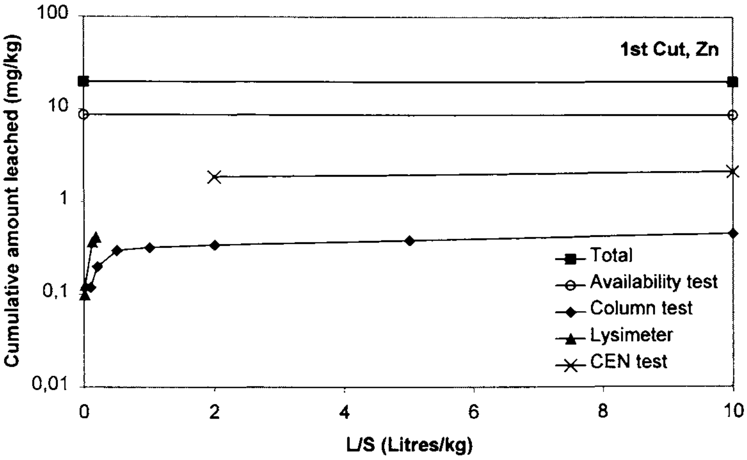

Figure 4f. Comparison of column-, CEN-, availability and lysimeter test. The cumulative leaching of Zn as a function of L/S.

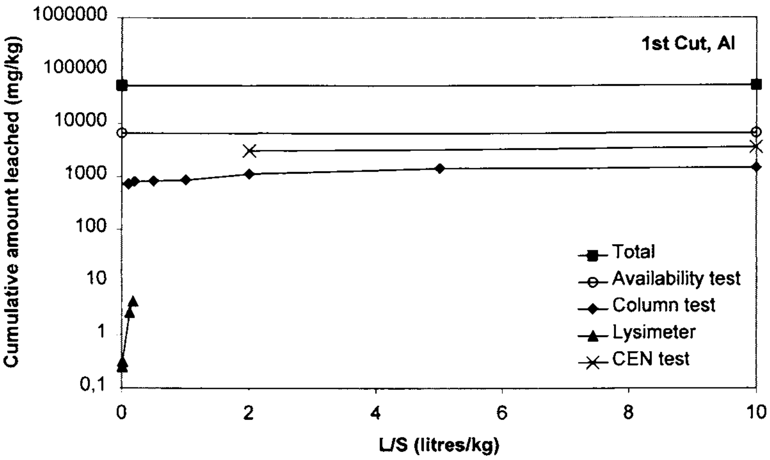

Figure 4g. Comparison of column-, CEN-, availability and lysimeter test. The cumulative leaching of Al as a function of L/S.

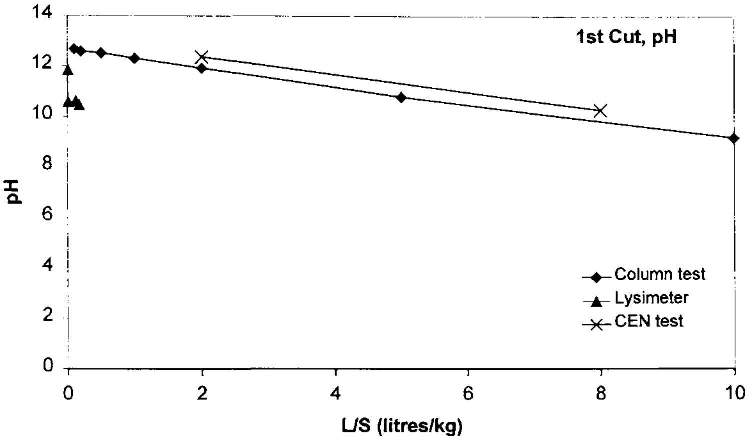

Figure 5. pH as a function of L/S for column-, CEN- and lysimeter test for 1st Cut, SPL waste.

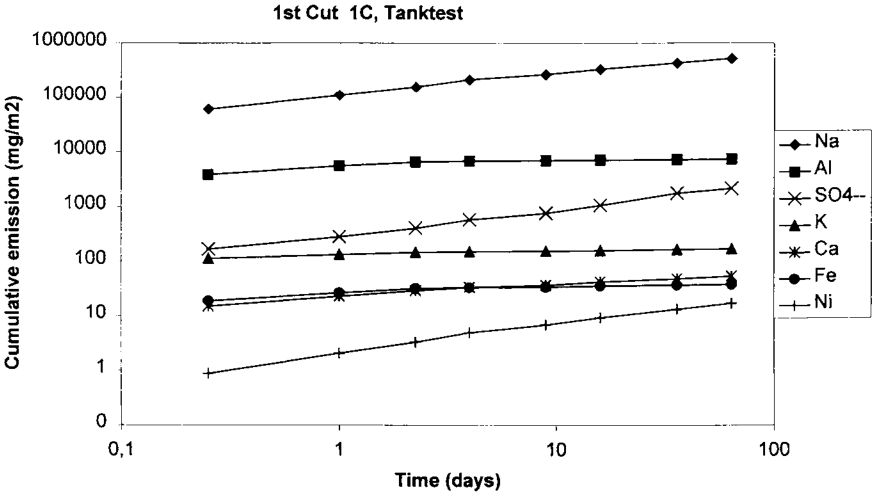

Figure 6. Release per surface area (mg/m^2) as a function of time of some major and trace elements observed in tank leaching test on 1st Cut SPL.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Speciation of metals in soil solutions - the concept of forced-shift-equilibrium: quantification of the complexing ability of soil solutions

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The concept of forced-shift-equilibrium makes it possible to model the degree of metal complexation in solutions without knowing the actual ligands in the sample. The experimental basis for the concept is the addition of increasing amounts of a chelating cation exchanger to a sample and a reference solution. By treating the ion exchanger as a reactant in the calculations, the complexing ability of the sample solution can be estimated. The concept is tested on two laboratory made solutions to determine the complexation of Cu by humate and of Cd by chloride.

1. INTRODUCTION

The uptake of elements in organisms depend on various soil and biological factors and it is normally assumed that the concentration of elements in the soil solution more closely determines the short term bioavailability than does the total content in the soil. More precisely - the chemical forms in which the elements are present in the soil solution determine the short term bioavailability.

To get a more reliable picture of the chemical forms of an element in a soil solution, it is necessary to perform a speciation study of the soil solution. When using computer modeling programs, such as MINTEQA2, SOILCHEM or PHREEQC, the significance of the organic content in the soil solution is not easily estimated. The composition of the organic matter is very complex and it behaves differently from soil to soil. To model its significance and behavior is therefore not an easy task. However, it is important to do so, because trace element chemistry and reactions in soil are closely related to the formation of stable complexes with organic substances.

The concept of forced-shift-equilibrium is a methodological concept designed to cope with this problem. The basis of the concept is the forced shift in equilibrium taking place in a solution when increasing amounts of a cation exchange resin are introduced. This shift in equilibrium can be measured by monitoring the concentration of the analyte in solution as a function of the concentration of active cation exchange resin sites added. A bulk property formation constant for the analyte to the complexing ligands in the solution can be calculated from this data. Given the bulk property formation constant for the complexation of the analyte in the sample, it is then possible to estimate the concentration of complexed analyte present in the solution.

In this paper the theoretical basis for this concept is described, and the approach will be demonstrated for two synthetic solutions to show the complexation of Cu by humate and Cd by chloride.

2. THEORY

Investigations using cation exchange resins for heavy metal speciation are widely reported. Several methods have been used to obtain information about the charge [1-2], thermodynamic stability and/or kinetic lability of complexes [3-6], or concentration of free (hydrated) ion in sample solutions [7-8]. In most cases Chelex-100 or a strong cation exchange resin have been used in such studies.

A fundamental problem with ion exchange is that it is not known how far the initial equilibrium between the various chemical forms is shifted by the ion exchange process itself [9].

Assuming that the simple hydrated ion gets exchanged very quickly, this exchange process will disturb the initial equilibrium in solution and result in the dissociation of thermodynamically weak and/or kinetically labile complexes. With increasing shift of the equilibrium by the ion exchange process the speciation result will be influenced even more by dissociation of various unidentified complexes [10].

In the proposed method this shift in equilibrium is used to estimate a formation constant for the complexation of the metal of interest with all the known and unknown complex forming species in the solution. Hence, the formation constant will be a bulk property formation constant for the solution and the metal of interest. The cation exchange resin is used as a competitive complexing agent; increasing amounts are added to force the equilibrium to shift in favour of the resin.

First, consider the solution without any complexing agents. When adding a cation exchange resin, the analyte will equilibrate with the resin according to equation 1.

$$dM + eX \Leftrightarrow M_dX_e \tag{1}$$

where M is the metal of interest, X is the complexing site of the resin, and M_dX_e is the metal bound to the resin. For the Chelex-100, the metal is assumed to interact in a 1 to 1 ratio, so that d=e=1. This gives:

$$K_x = \frac{(MX)}{(M)_f(X)} = \frac{(M)_x}{(M)_f(X)} \tag{2}$$

$$\Rightarrow (M)_f = \frac{(M)_x}{K_x(X)} \tag{3}$$

$$\Rightarrow \frac{(M)_x}{(M)_f} = K_x(X) \tag{4}$$

where $(M)_f$ is the concentration of free metal in solution in equilibrium with the ion exchange resin and $(M)_x$ is the concentration of metal bound to the cation exchange resin. (X) is the concentration of the complexing sites of the resin (number of equivalents of sites per volume) and K_x is the formation constant.

(X) is given by the equation:

$$(X) = (X)_0 - \sum (M)_x \tag{5}$$

where $(X)_0$ is the estimated added amount of resin equivalents.

$(M)_x$ can be calculated from:

$$(M)_x = (M)_{TOT} - (M)_f \tag{6}$$

where $(M)_{TOT}$ is the total concentration of the metal present.

Now, consider a sample solution with a complexing ligand:

$$aM + bL \Leftrightarrow M_aL_b \tag{7}$$

where L is the ligand with complexing properties. The formation constant, K_L, will be:

$$K_L = \frac{(M_aL_b)}{(M)_f^a(L)^b} = \frac{(M)_c}{a(M)_f^a(L)^b} \tag{8}$$

$(M)_c$ can be calculated from:

$$(M)_c = (M)_{TOT} - (M)_f - (M)_x \tag{9}$$

where $(M)_c$ is the concentration of metal bound as complexes in solution.

$(M)_x$ can be calculated from:

$$(M)_x = (M)_{TOT} - \left[(M)_f + (M)_c\right] \tag{10}$$

where $[(M)_f + (M)_c]$ is the total measured concentration of metal in the solution.

If (L) is assumed to be constant ((L)>>(M)), it may be incorporated in the formation constant:

$$K_L^{'} = K_L (L)^b = \frac{(M)_c}{a(M)_f^a} \tag{11}$$

This is an assumption, which is not necessarily true. However, it is an assumption that can be made as a first approximation.

When adding increasing amounts of a cation exchange resin, the equilibrium between the different ligands and the metal will be shifted in favour of the resin. Provided the complexing ability of the ion exchange resin is known, the complexing ability of the sample solution (expressed as a bulk property formation constant) can be estimated from the last equation. To do this, the concentration of metal in the reference solution $(M)_f$ is measured and the metal adsorbed to the resin $(M)_x$ is calculated by difference (eq. 6). $(M)_x/(M)_f$ is plotted against the free resin concentration (X) and K_x is calculated from the slope of the linear fit of the scatter plot (eq. 4). Then the concentration of metal in the sample solution $[(M)_f+(M)_c]$ is measured, the concentration of free metal in solution $(M)_f$ is calculated from eq. 3 and the concentration of complexed metal in solution $(M)_c$ is calculated by difference (eq. 9). Then an estimation of K'_L can be made from eq. 11.

3. EXPERIMENTAL

3.1. Reagents

1000 mg/l solutions of Mg, Cd and Cu in 2-5 % nitric acid (Teknolab) are used in the experiment. The humate originates from a sodium salt of humic acid (Aldrich). A 1 g/l solution of the humate was made six months before the experiment and used as a stock solution. NaCl was used for chloride addition and NaOH and nitric acid for pH-adjustments. Methanol is used for the resin suspensions. All reagents are of pro analysi purity and the water used is double distilled. The resins used are Chelex-100 (200-400 mesh, BioRad Laboratories), and polystyrene cross-linked with divinylbenzene (200-400 mesh, Acros).

3.2. Apparatus

0.45 μm non-sterile syringe filters are used for filtration (Sartorius Minisart RC 25). All bottles are made of polyethylene. A Metrohm 736 GP Titrino is used as a pH-stat, and a shaking table is used for long-time shaking. For the element determinations an inductively coupled plasma atomic emission spectrometer is used (ICP-AES; Termo Jarrel Ash, Iris Advantage).

3.3. Procedure

A 5000-fold (w/w) dilution of the Chelex-100 resin is made by adding 25 g polystyrene resin to 0,005 g Chelex-100. The resin mixture is transfered to a polyethylene bottle and shaken with 50-60 ml of 20% methanol in distilled water for at least two hours. The resin suspension is allowed to settle before use and is stored at 4°C.

Table 1
The composition of the solutions analysed.

	Reference solution	Humate solution	Chloride solution
Cu and Cd	100 μg/l	100 μg/l	100 μg/l
Mg	10 mg/l	10 mg/l	10 mg/l
Na-Humate		10 mg/l	
NaCl			1,16 g/l
pH	6.04	5.97	6.01

A reference solution, a humate containing solution and a chloride containing solution are made as specified in Table 1. All solutions are pH-adjusted with aqueous NaOH to pH 6.0 with a pH-stat and given 1 day of equilibration time before the experiment is continued, to allow for the slow kinetics of humic-metal interactions [11].

For each solution the following is done: 15 aliquots of 10-15 ml are introduced to 25 ml screwcap bottles of polyethylene. A volume of resin suspension (0 – 2000 μl) is added to each aliquot, to cover the range from 0 to 0.015 meq/l of Chelex-100. The resin capacity is estimated from the wet volume. All aliquots are then placed on a shaking table and shaken at 100 Hz for 20 hours. The resin phase is then separated from the liquid phase by filtration with a 0.45 μm syringe filter. The liquid phase is acidified with nitric acid before Cd and Cu are determined with ICP-AES.

4. RESULTS

In order to estimate the parameters required to model the forced shift in equilibrium taking place when adding increasing amounts of the ion exchange resin, the following is done:

4.1. Estimation of K_x from the reference solution

In figure 1 and 2, the ratio $(M)_x/(M)_f$ for Cu and Cd respectively, is plotted as a function of the concentration of free Chelex-100 resin sites remaining in suspension (X) (eq. 5). A linear fit forced through 0 gives a slope corresponding to K_x (eq. 4). It can be seen from equation 4 that the ratio $(M)_x/(M)_f$ becomes zero when the concentration of free resin sites approaches zero. Hence, the curve was forced through the origin.

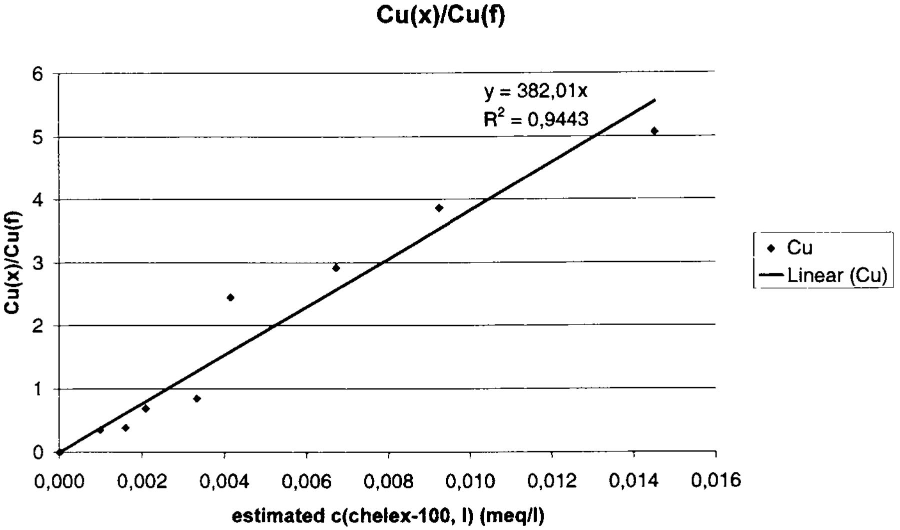

Figure 1. The ratio of Cu between the resin phase and the solution [$(Cu)_x/(Cu)_f$] for the reference solution plotted against the amount of free resin present in suspension (X). The slope of the linear fit equals the dissociation constant (K_x) of the free metal to the resin.

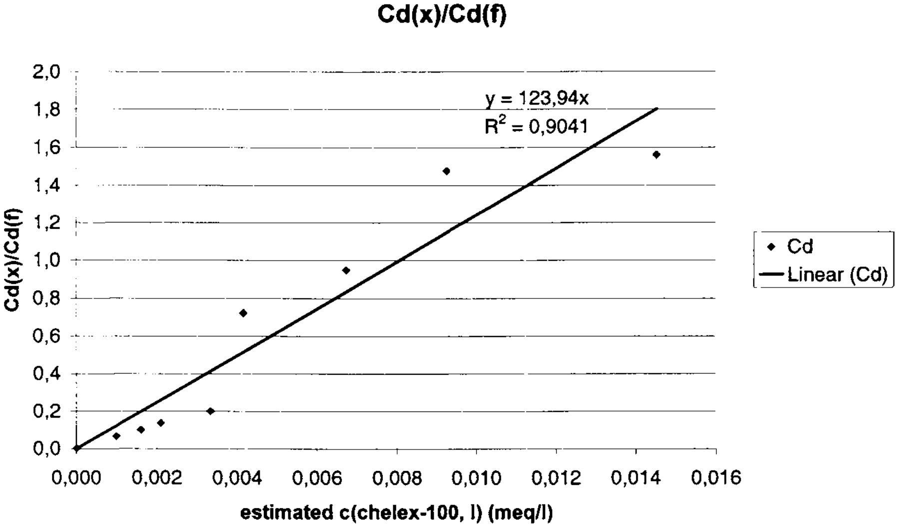

Figure 2. The ratio of Cd between the resin phase and the solution [$(Cd)_x/(Cd)_f$] for the reference solution plotted against the amount of free resin present in suspension (X). The slope of the linear fit equals the dissociation constant (K_x) of the free metal to the resin.

4.2. Estimation of 'a' and K'_L from the sample

For each point in the data set $(M)_x$ is calculated from eq. 10. From $(M)_x$ and K_x, the concentration of free noncomplexed metal $(M)_f$ is calculated (eq. 3). The concentration of complexed metal $(M)_c$ is given from eq. 9. These concentrations are used to estimate the K'_L for different values of *a* (eq. 11). Then the relative standard deviation (RSD) for the K'_L values (calculated for each point in the data set) are plotted against *a* in order to find the value of *a* that gives the lowest RSD (figure 3). In order to make the set of equations converge, all outliers had to be excluded. To make a well defined set of criteria for this exclusion, further work needs to be done. In order to have a meaningful mathematical use of equation 8, *a* needs to be larger than zero. Because K'_L is a function of *a*, the RSD of K'_L calculated for each point in the data set of $(M)_c$ and $(M)_f$ (eq. 11) should have a minimum. Given this value of *a*, the concentration of complexed metal $(M)_c$ is plotted against $a(M)_f^a$. A linear fit forced through 0 (see above) gives a slope corresponding to K'_L (eq. 11). The linear fit is shown in figure 4 and 5 for Cu and Cd respectively.

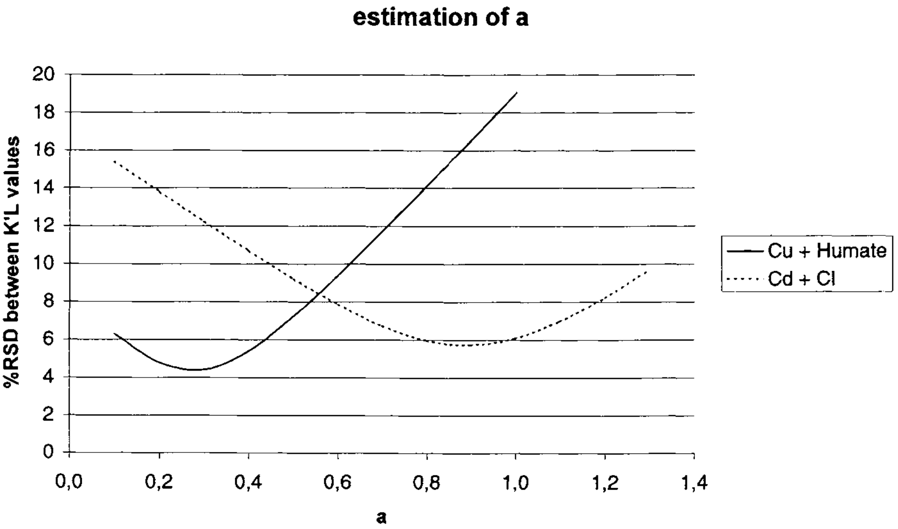

Figure 3. The relative standard deviation of K'_L-values calculated for each measurement plotted against a, given that $K'_L=(M)_c/a(M)_f^a$.

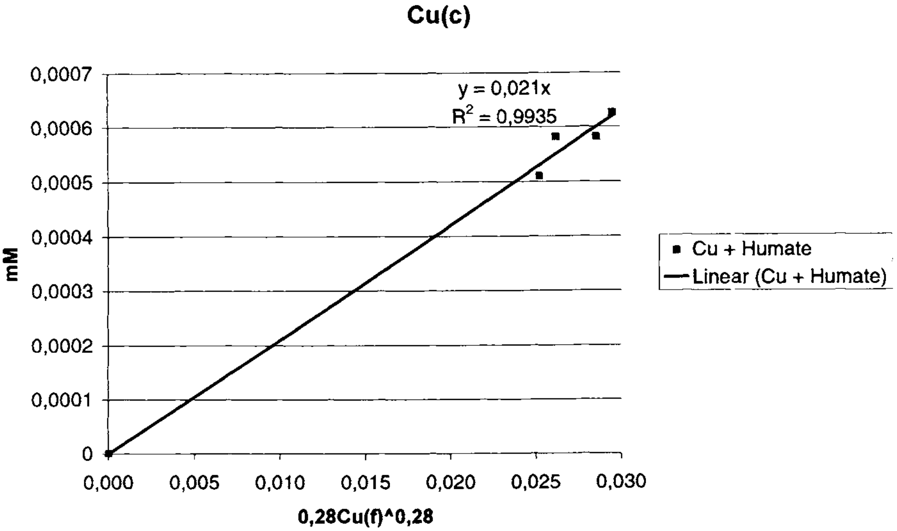

Figure 4. The calculated concentration of complexed Cu, $(Cu)_c$, plotted against the concentration of free Cu in solution according to $a(Cu)_f^a$, given a = 0.28. The slope of the linear fits equals the formation constant for the complex $(K'_L=(M)_c/a(M)_f^a)$.

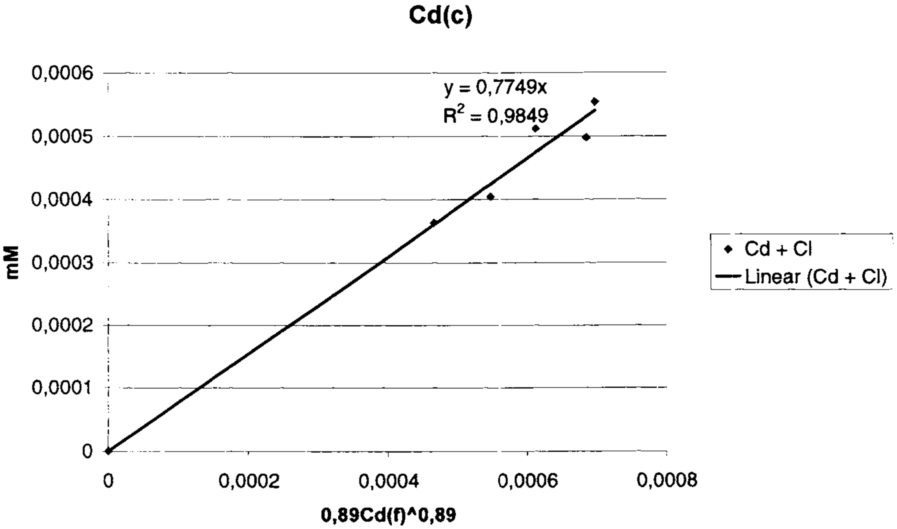

Figure 5. The calculated concentration of complexed Cd $(Cd)_c$ plotted against the concentration of free Cd in solution according to $a(Cd)_f^a$, given a = 0.89. The slope of the linear fits equals the formation constant for the complex $(K'_L=(M)_c/a(M)_f^a)$.

Table 2
A summary of the estimated parameters K_x, a and K'_L and the estimation of relative amount of complexed metal in the solutions.

complex	K_x	*a*	K'_L	% complexed metal in solution
Cu-Humate	382.01	0.28	0.021	54 (as Cu)
$CdCl_x$	123.9	0.89	0.7749	63 (as Cd)

Given K_x and K'_L and *a*, the forced shift in equilibrium taking place when increasing amounts of ion exchange resin is added can be modelled, and the amount of complexed metal in solution without any ion exchange resin present can be numerically estimated. A summary of the estimated parameters is given in table 2.

In figure 6 and 7 the normalized concentrations of Cu and Cd in the different aliquots of the solutions are shown plotted against the estimated concentration of free resin sites. The unbroken lines represent the reference solution with no complexing ligands. The broken lines represent the sample solutions with humate (for Cu) or chloride (for Cd) present.

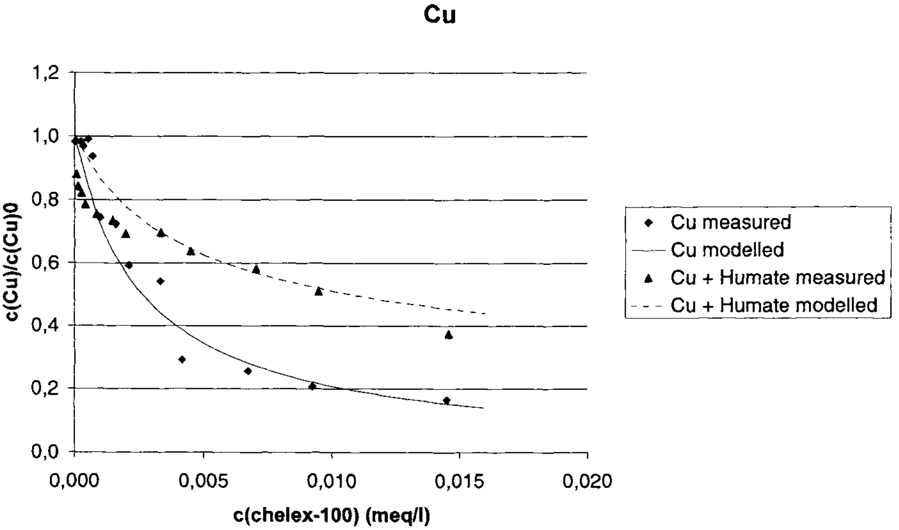

Figure 6. Normalised concentration of Cu $[(Cu)_l/(Cu)_0]$ plotted against the amount of free resin in suspension (X). The unbroken line represents a reference solution, and the broken line a sample solution containing humate. The total Cu-concentration is approximately 100 µg/l. The pH of the solution is 6.0, and the concentration of humate is 10 mg/l as Na-Humate.

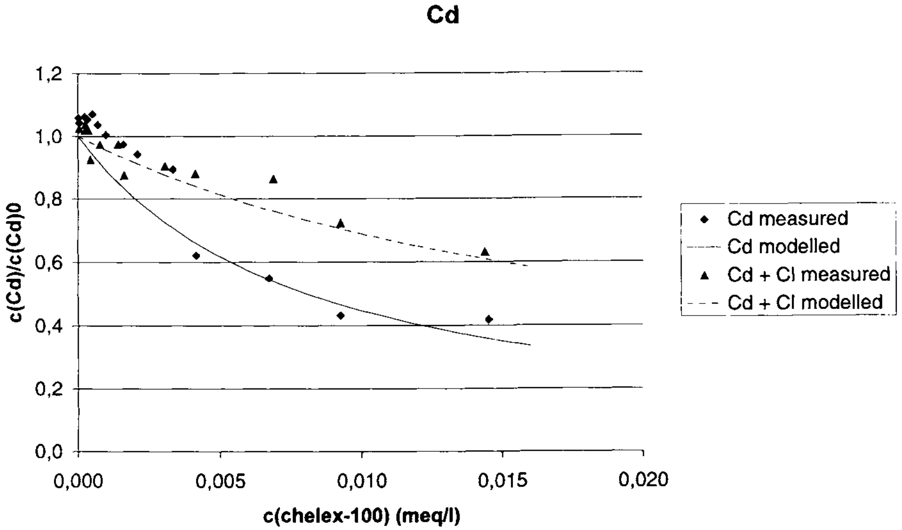

Figure 7. Normalised concentration of Cd [$(Cd)_l/(Cd)_0$] plotted against the amount of free resin in suspension (X). The unbroken line represents a reference solution, and the broken line a sample solution containing chloride. The total Cd-concentration is approximately 100 μg/l. The pH of the solution is 6.0, and the concentration of chloride is 1.16 g/l as NaCl.

Since the concentration of analyte is higher in the sample solution than the in the reference solution with increasing amounts of Chelex-100, the ability of the resin to bound the analyte in the sample solution is lower than in the reference solution. This can only be explained by the presence of at least one competing complexing agent in the sample solution. Hence, the figures show a clear evidence for complexation of Cu by humate and Cd by chloride. No complexation was indicated for Cu by chloride and for Cd by humate (results not shown).

4.3. Cu and Cu-humate

It is a fairly good correlation between the measured data points and the estimated line describing the distribution of Cu between solution and resin with no ligands present (figure 6, unbroken line). The model describing the distribution when humate is present as a complexing agent (broken line) shows good agreement for concentrations of free resin sites larger than 0.003 meq/l. It can be seen from figure 6 that for smaller amounts of resin the model fails to agree with the experimental data. This may be caused by analytical errors due to the small amounts of resin added. It is anyhow difficult to explain that the introduction of a complexing agent enhances the ability of the ion exchange resin to complex metals. This could only be possible if the humate complex adsorbs to the resin. If this occurs, this effect should increase with increasing amounts of resin, which is not the case. An experiment where the polystyrene resin is used without diluted Chelex-

100, shows no significant adsorption of Cu (or Cd) to the resin phase. Hence, it is more likely to originate from analytical difficulties rather than being a result of adsorption effects. The model suggests that 54% of the Cu in the sample solution is complexed with the humic material at pH 6.

4.4. Cd and $CdCl_x$

It is a fairly good correlation between the measured data points and the estimated line describing the distribution of Cd between solution and resin with no ligands present (figure 7, unbroken line). As for Cu, the model fails for concentrations of free resin sites less than 0.003 meq/l. In addition to analytical uncertainties, this may be caused by the competing ion exchange introduced by Cu, and insufficient correction of this when calculating the concentration of free resin sites. A value of a less than but close to 1 probably means that most (but not all) of the complexed Cd is complexed with chloride as a one-to-one complex ($CdCl^+$), which is in agreement with established thermodynamic data. The solution was modeled with PHREEQC using the WATEQ4F database. According to this, 53% of the Cd should be present as chloro-complexes. The numerical estimation of the complexed amount of Cd in solution using the model described gives a value of 63%. This overestimation may be a result of the Cu competition in the system. If this is not sufficiently corrected for in the calculation of free resin sites present in the suspension, the estimation of K_X, and K'_L will be influenced.

5. CONCLUSIONS

The concept of forced-shift-equilibrium makes it possible to estimate the degree of metal complexation in solutions without knowing the actual ligands present in the sample. The use of a strong chelating ion exchanger may be used to study the complexation of metals with the ligands in the solutions, provided that it is only added in very small amounts. The methodology succeeds fairly well on $CdCl_x$ speciation, which by other authors [12] have been stated as very difficult when using Chelex-100. The results show, however, that further work needs to be done to improve the calculations.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Seven years of experiences with lysimeter leaching of pulverised fuel ash

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In the Netherlands the leaching behaviour obtained by the Dutch Column test is decisive if and in what way the by-products can be used as a building material or in what way the waste has to be dumped. Accordingly, the translation of results of the Dutch standard leaching tests into field conditions is important and therefore a major research area at KEMA.

In the leaching process two steps can be considered: percolation and dissolution of various water-soluble compounds. Only through the combination of these two processes compounds can be leached out of the waste and enter into the environment. In order to study these processes under field conditions in detail, lysimeters with a height of 1-m and 4-m were built and filled with pulverised fuel ash produced by Dutch coal-fired power plants. In these lysimeters the moisture content was monitored and the vaporisation of the moisture determined. The hydrology was modelled. In order to gain more insight into the chemical processes, the pore water in the lysimeters and the percolate was analysed as well.

In this paper the results of the first seven-years of the experiment are summarised. The L/S depends on the height of the lysimeter and amounts after six years to 1,5 L•kg^{-1} for the low lysimeter and 0,5 L•kg^{-1} for the high lysimeter. The leaching of the lysimeters is compared with the laboratory leaching tests for the same L/S value. It appears that the leaching of Si and B in the lysimeters is comparable as in the column test. The same observations are also found for Mo, Cr and Se, if only the low lysimeter is taken into account. However, the leaching for Mo, Cr and Se is higher in the high lysimeter with respect to the column test. The leaching of Ca, Fe, Mg, Ba, Cu and Sb in the lysimeters is lower than in the column test. The leaching of Al, V, K and Na in the lysimeters is higher than in the column test, besides the leaching in the high lysimeter is higher than in the low lysimeter. The differences between laboratory tests and lysimeters are ascribed to the different time scale. Most probably the observed differences are kinetically determined.

Due to meteorological circumstances in the upper part of the lysimeters dry-wet cycles were observed. It appears that when the PFA became wet again, every time peak leaching of Ca, S, Mo and Se was observed.

1. INTRODUCTION

In the Netherlands electricity is nowadays mainly generated using natural gas and coal. In the eighties the contribution of coal increased from about 10% to about 40% (from about 2 million metric tons to about 9 million metric tons yearly). Only imported bituminous coal is fired. Coal is imported from all over the world. Major suppliers are South Africa and Colombia. Other suppliers are Australia, Indonesia, Poland and USA. Today mostly blends are fired. In the Netherlands the only boilers installed are pulverised coal-fired dry bottom types. The flue gases are cleaned by high-efficiency cold-side electrostatic precipitators (ESPs) and by flue-gas desulphurization (FGD) installations of the lime(stone)/gypsum process. The by-products are bottom ash, collected ESP ash, gypsum and sludge from the wastewater treatment plant. The collected ash from the electrostatic precipitators (ESP's) will hereafter be called pulverised fuel ash (PFA).

The policy in the Netherlands is in principle not to produce waste, but to produce usable residues. Long-term disposal of coal-firing residues is currently impossible. The electricity generating companies in the Netherlands founded a special firm for the marketing of the coal-firing residues: 'de Vliegasunie' (Dutch Fly Ash Corporation). This firm also stimulates research and experiments with applications. So far the Dutch Fly Ash Corporation has realised almost 100% utilisation of all by-products.

The Dutch Decree on Building Materials is decisive for the application of the by-products. Limits for leaching of elements and compounds are set in this decree. The leaching behaviour at L/S=10 has to be determined by the Dutch Column test. If the by-products fail to meet the limits, there are two options: immobilisation or storage. The results of the Dutch Column test at L/S=1 determines also the lay out of the storage.

Accordingly, the translation of results of the Dutch standard leaching tests into field conditions is important and therefore a major research area at KEMA. For 16 years at the KEMA premises leaching of PFA has been studied in lysimeters. In this paper the results for 5 lysimeters, built at the end of 1992 and thus almost seven years in operation, are discussed. The experiments are still ongoing.

2. LEACHING OF PULVERISED FUEL ASH UNDER FIELD CONDITIONS

2.1. Aim of the lysimeter experiments

In the leaching process two steps can be considered. The first step is transport of water along the pores, so called percolation. The second step is the dissolution of various water-soluble compounds. Only through the combination of these two processes can compounds be leached out of the waste and enter into the environment. In leaching tests there is always a good contact with water, and actually only the dissolving and precipitation process is tested. The question arises how much water percolates under field conditions and how much rainwater will be evaporated.

As there were strong indications from a four-year trial storage project of PFA, with no cover layer, at the Amer power station that the initial moisture level did not increase over the years, it was decided to study this subject in detail. The conclusion was that evapotranspiration could be a very important parameter, so the estimation of evapotranspiration rates must be quantified. The only reliable way of measuring actual evapotranspiration is to use large containers, called lysimeters, evaluate the different components of the water balance precisely, and calculate the evapotranspiration by subtraction. Lysimeters are meant to be a set up for studying the hydrology of soils. The height of the lysimeter is an important parameter, therefore lysimeters were built with a height of about 1 meter and about 4 meter. The lysimeter of 1 meter can be compared with other lysimeters with the same height at the KEMA premises, which were in operation for 10 years at that time.

The percolate is monitored in order to compare the results of the laboratory test with the results obtained with the lysimeters under field conditions. To get more insight into the mechanisms of dissolution and precipitation, the pore water is monitored as well. Percolate and pore water are analysed for elemental composition (Ca, Cl, Fe, K, Mg, Na, S, Si, As, B, Ba, Br, Be, Cd, Co, Cr, Cu, F, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, V, W, Zn, CO_3, SO_4, TIC, TOC), pH, Eh (redox), Ec (conductivity) and chemical speciation of arsenic, chromium and selenium.

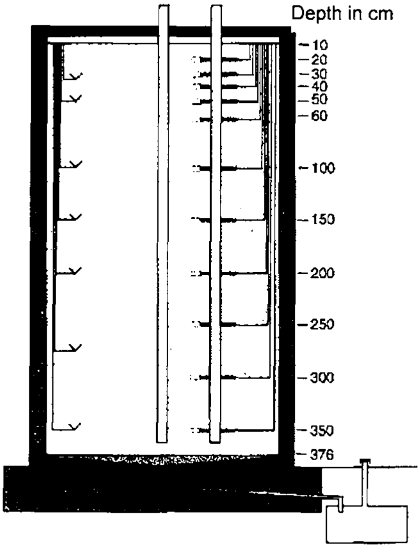


Figure 1. Cross section of the large lysimeter; points indicated at the left side are for taking samples of pore water, the vertical tubes and the points at the right side are for determining the moisture content.

2.2. Experimental

Five lysimeters were built (Ø = 2m, four of about 4 m in height and numbered 1, 2, 3 and 4 (see Figure 1) and one of about 1 m in height, numbered 5, filled with pulverised fuel ash produced by Dutch coal-fired power plants. During the filling samples were taken for determining the bulk density (1006 $kg \bullet m^{-3}$ on a dry basis) and the initial moisture content (7.7 v/v %) at several heights. From two grab samples the chemical composition, particle size distribution (MMD = 15μm), proctor test (density as a function of the moisture content: the maximum dry density is 1184 $kg \bullet m^{-3}$ at a moisture content of 30.3 %), specific density (2200 $kg \bullet m^{-3}$), water-retention characteristics and shrink were determined.

The moisture content was measured originally weekly, and nowadays once in the two months, with a neutron probe at various heights. Pore water is sampled at various heights (see Figure 1) by means of a membrane. In the course of time these membranes got obstructed. At the start of the experiment samples were taken at six depths but now only two membranes are still working. The pH, Eh and conductivity are measured on line in the pore water. Secondly, percolate is collected and analysed in two ways: in fresh collected samples and each time before the tank was emptied (so far four times). Furthermore the precipitation is being monitored.

2.3. Laboratory leaching tests

The leaching behaviour of PFA, as used in the lysimeters, was studied in detail at the laboratory. Besides the Dutch Column (L/S=10) test and the Dutch availability (L/S=100) test,

Table 1
Precipitation on the lysimeters

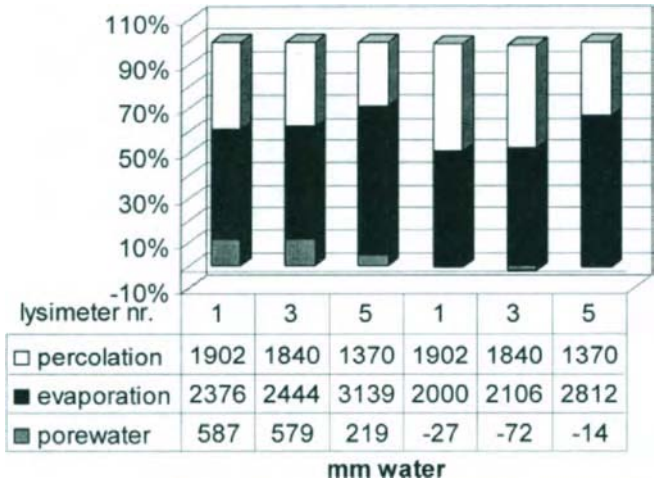
Year	mm
1993	**872**
1994	**986**
1995	747
1996	*489*
1997	*620*
1998	**920**
1999	770
mean	772$^{1)}$

$^{1)}$ 30 years average is 750 mm

the Dutch Shaking (Cascade) test (L/S=100) and US EPA test (L/S=20) were carried out as well. The availability test was carried out three times: for the original sample, after the column test and after the cascade test. The results are described and discussed in reference 1.

2.4. Hydrological results of the first seven years

The bulk density is an important parameter for the hydrology. The bulk density of the PFA in the lysimeters approximates the maximum as obtained in the proctor test as performed at the laboratory. This bulk density is also in agreement with the density in an actual storage site. At the laboratory also the water retention characteristics (desorption) were determined. The obtained characteristics are comparable to those of other pulverised fuel ashes, as produced in the USA and also comparable to coarse sand [1]. However, the critical pressure head for coarse sand is about 1 m and for PFA it is about 3.5 m. Theoretically, moisture at depths up to 3.5 m can be transported and evaporated. Therefore, it seems vital that the lysimeters are higher than 3.5 m.



lysimeter nr.	1	3	5	1	3	5
□ percolation	1902	1840	1370	1902	1840	1370
■ evaporation	2376	2444	3139	2000	2106	2812
▨ porewater	587	579	219	-27	-72	-14

Figure 2. Water balance of the lysimeters nr.1, 3 (both high) and nr.5 (low)

It appeared that the maximum saturation of PFA under laboratory conditions, as well as in the lysimeter under field conditions, is about 53%. Percolation can occur only if the maximum saturation is accomplished. For the low lysimeter (0.95 m) it took 193 days and for the high lysimeter it took 427 days before saturation occurred and percolation started. The low lysimeter was completely saturated whereas the high lysimeter was only saturated for the lowest part for about 1 meter. In the latter case this is called "hangwater", a well known phenomenon in soil hydrology. The upper layer of the high lysimeters is almost never saturated. The moisture content depends on the meteorological conditions and varies between 25% and 35%. The high lysimeter is to be considered as a soil in which the ground water level (the upper surface of the saturated zone) lies at 2.8 m depth.

In the observed period the meteorological conditions were extreme. The years 1993, 1994 and 1998 were extremely wet years, whereas the years 1996 and 1997 were relatively dry for the

Dutch climate. Over the whole period the yearly averaged precipitation amounts 770 mm, which is comparable to the 30 years average precipitation of a nearby meteorological station of 750 mm per year (see Table 1).

Evaporation depends on the degree of saturation. In the starting period there was no saturation and therefore the evaporation was less than in the period with saturation. Because in the long term the starting period is negligible, the evaporation of the period after saturation is more representative: 52-54% of the high lysimeter and 67% of the low lysimeter. The relative contributions of evaporation, percolation and changes in pore water amount for the whole period and after saturation are given for the lysimeters 1, 3 and 5 in Figure. 2. The hydrology of lysimeters 4 is not measured any more, where as lysimeter 2 is used for experiments with NaCl, after which the hydrology deviates from the other lysimeters.

The percolation over the whole period is also given in Figure 2. It appears that 38-39% of the precipitation effectively percolated through the lysimeter of 3.8 meter and 29% of the precipitation through the lysimeter of 0.95 meter. In the long term the period after saturation is more representative: about 53% percolation with a height of 3.8 meter and about 33% with a height of 0.95 meter.

The Building Decree estimates a fixed amount of percolate of 300 mm per year, which is an average of 39% of the Dutch precipitation. From the results obtained in this project it can be concluded that so far the figures as used in the Building Decree gives a good approach of the reality.

2.5. Chemical results of the first seven years

The chemical composition of pore water at various heights in lysimeter 3, the percolates of lysimeters 1, 3 and 5, and the tank-water of lysimeter 1, 3 and 5 were measured regularly. Not all elements as listed in 2.1 were measured each time in all samples. The difference between percolate and the tank-water sample is that the percolate was freshly sampled directly from the lysimeter and gives the results from a point measurement, whereas the tank-water samples were obtained from the collection tank, which represent the accumulated percolate. These latter analyses were done only when the tank was full.

As an example, the results for sulphate, mostly from lysimeter 3, are given in Figure 3. In Figure 3a, 3b and 3c the sulphate concentrations along the y-axis are given as a function of the time in months, as indicated along the x-axis. Figure 3a and 3b represent the sulphate concentrations in the pore water at a depth of 0.5 m and 2 m respectively. Figure 3c represents the sulphate concentrations in the freshly obtained percolate. In Figure 3d the same sulphate concentrations as in Figure 3c are given, but now along the x-axis the L/S ratio is given. This has been done because in Figure 3d also the sulphate concentrations in the percolate of the low lysimeter, number. 5, is given and by applying the L/S scale the results of both lysimeters can be compared. Finally in Figure 3e, 3f and 3g some hydrological data are given. On the x-axis of Figure 3e and 3g the amount of water in mm is given and on the Y-axis the time in months. Figure 3e gives the precipitation and Figure 3g the amount of the percolate. In Figure 3f the moisture content, given in percentage, in the pore water at a depth of 0.4 m and 2.2 m is given. Form Figure 3 the following remarks can be made:

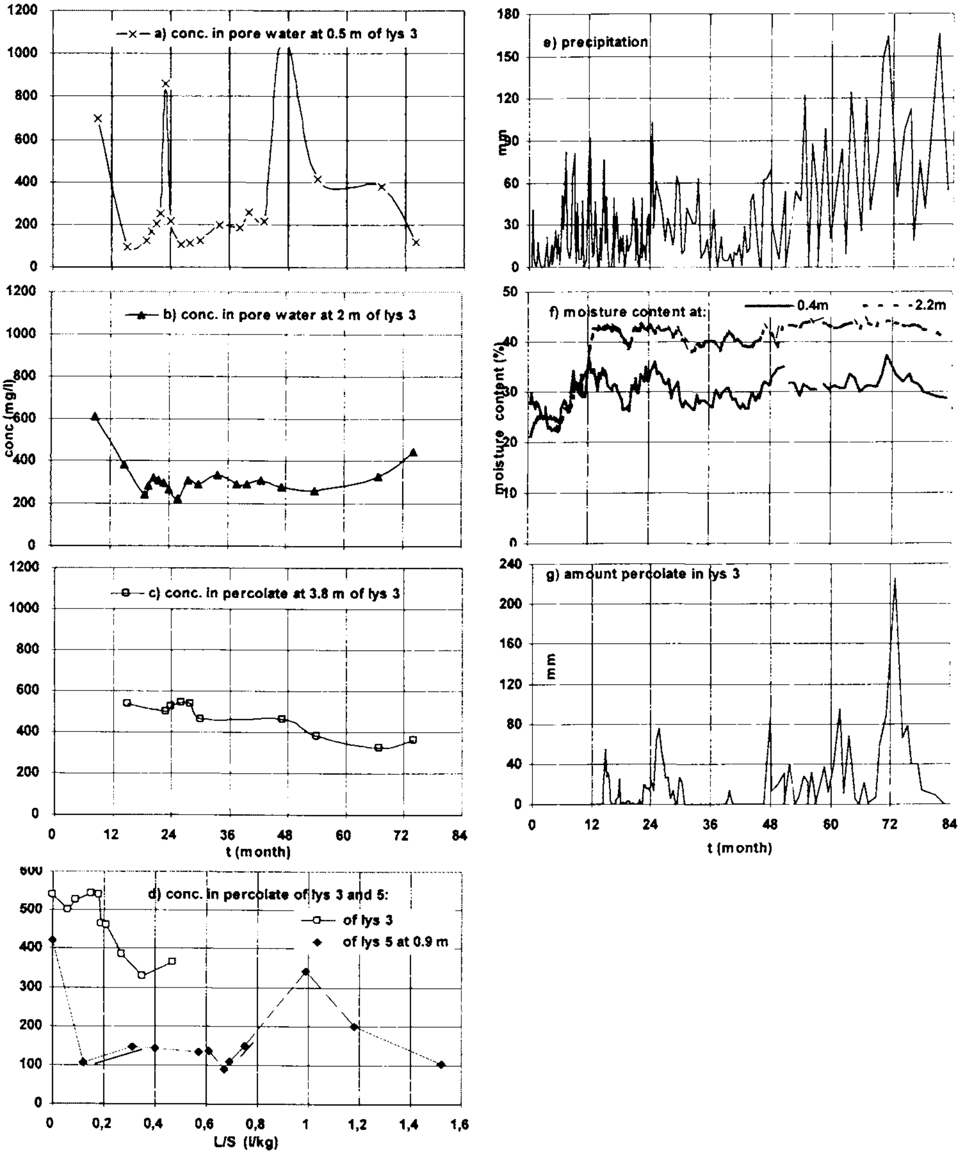


Figure 3. Sulphate concentrations and hydrological results. Sulphate concentrations in a) pore water at 0.5 m, b) pore water at 2 m, c) in percolate of lysimeter 3, d) in percolate of lysimeter 3 and 5 as a function of L/S. Hydrological results in e) precipitation, f) moisture content at 0.4 and 2.2 m and g) amount of percolate for lysimeter 3.

a) The sulphate concentrations increase going from top to bottom: 0.5m→2m→3.8m (=percolate) which corresponds on average with about 200, 300 and 450 mg•L^{-1}; thus going down more and more sulphate is dissolved.

b) In principle the highest concentrations are found in the very beginning (peak leaching), afterwards the concentrations decrease rapidly in time. This phenomenon was also found in the percolate of lysimeter 5 but not found in the percolate of lysimeter 3. The effect of peak leaching is steadily decreasing by going down in the large lysimeter.

c) The pore water content increases in the first year until a kind of equilibrium is reached; about 45% at the bottom and about 30% at the top of the lysimeter (Figure 3f). However in dry periods the pore water content decreases temporally. The first time that this phenomenon occurs was after 560 days, in the summer of 1994. It is observed at all levels, however the effect decreases from top to bottom. The minimum at the bottom occurs 47 days later than that at the top. It appears, that when afterwards the pore water content increased again to normal levels, the sulphate concentrations increased enormously again. So the peak leaching started again. This effect for sulphate was well visible at 0.5m. The same effect is also detected after about 48 months. Due to financial constraints the interval between the measurements was changed during the years from once a month, to once in three months, to once a year (see Figure 3). This means that the chance of detecting the above-described effects is reduced. Calcium shows the same pattern as sulphate, so it is concluded that calcium is associated with sulphate, most probably as gypsum.

d) The variation in concentrations becomes less by going from top to bottom. This is also visible by comparing the concentrations of the percolate of the high lysimeter 3 and the low lysimeter 5 (Figure 3d). The pattern of sulphate concentrations in the percolate of lysimeter 5 resembles the concentrations in the pore water at 0.5 m in lysimeter 3. In order to compare the leaching of sulphate in lysimeter 3 with lysimeter 5 properly along the x-as the L/S ratio in stead of the time is given.

In Figure 4 for molybdenum the same graphs as for sulphate are given. The same pattern is observed, however the peak leaching after dry/wet cycles is much less pronounced. The explanation might be that there is less molybdenum than sulphate. This could mean that most of the molybdenum is already leached in the beginning.

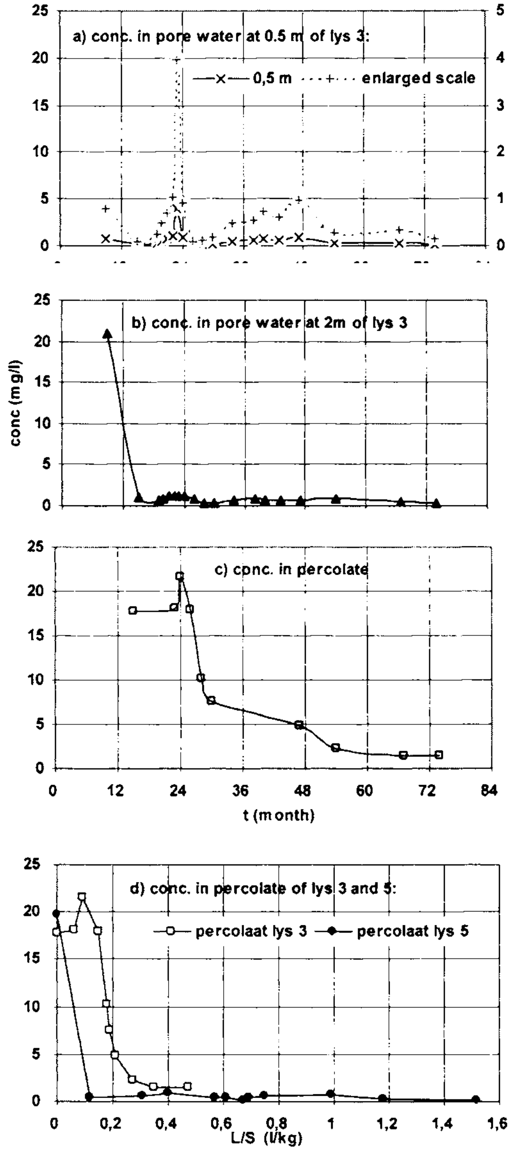


Figure 4. Molybdenum concentrations in a) pore water at 0.5 m, b) pore water at 2 m, c) in percolate of lysimeter 3, d) in percolate of lysimeter 3 and 5 as a function of L/S

2.6. Speciation

For the elements arsenic, selenium and chromium the speciation is also measured in a few samples pore water, percolate of the lysimeters and percolate of the column test at the laboratory. In all cases all chromium was present as Cr(VI) and all arsenic as As(V). Therefore these measurements are not performed any more after 1994.

For selenium the results are complex. In the percolate obtained at column test all selenium was present as Se(IV). In the first collected percolate of the high lysimeters (nr 1, 2, 3 and 4) all selenium was also present as Se(IV). However in the pore water of the high lysimeter and in the first collected percolate of the low lysimeter (nr. 5) selenium was present for about 20% as Se(IV) and for about 80% as Se(VI). In the pore water first only Se(VI) is present, but in the upper part the lysimeter, Se(IV) increases in time. A possible explanation is that a small part of Se is present as Se(VI) due to oxidation in the upper layer, as the redox potential is higher near the surface in contact with air. This fraction is very mobile and is rapidly removed.

The peak leaching after a dry/wet episode is also found for Se(VI). After 23 months when the second peak leaching pattern occurred, 90% of the selenium in the pore water at 0.5 m consist of Se(VI). One month later the fraction of Se(VI) was decreased to 77% and 7 months later to 66%. The absolute Se(IV) concentrations stayed constant. In the pore water at the lower part of the lysimeter and in the percolate, Se(VI) decreased from 90% to 80%.

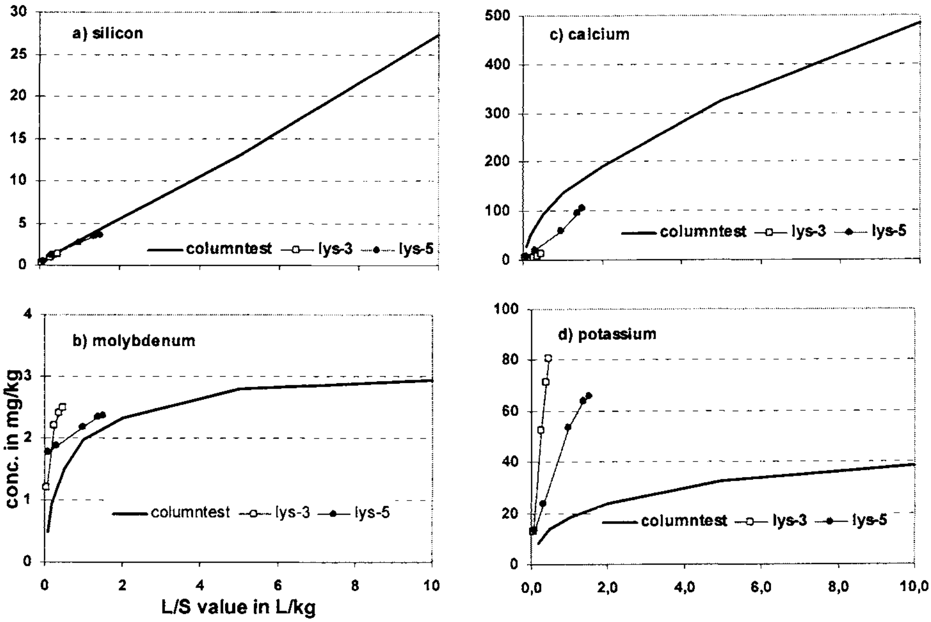


Figure 5. Cumulative leaching behaviour in the column test, in the high lysimeter (nr. 3 ~4m) and in the low lysimeter (nr. 5 ~1 m)

3. COMPARISON OF LEACHING BEHAVIOUR IN THE COLUMN TEST AND IN THE LYSIMETER

In Figure 5 the cumulative leaching behaviour in the column test and in lysimeters 3 (3.8 m) and 5 (0.95 m) are given for four elements: silicon, molybdenum, calcium and potassium. Each element represents a group of elements showing similar behaviour, which will be discussed below.

a) The first group contains elements, which show a comparable degree of leaching in the column test as under field conditions for both lysimeters. The elements Si and B belong to this group.
b) To the second group belong elements for which leaching in lysimeter 5 shows a similar behaviour as in the column test, but which show a higher degree of leaching in lysimeter 3.The peak leaching under field conditions is much more pronounced compared to the column test. Probably the cumulative leaching at L/S 10 under field conditions will be comparable to the cumulative results at L/S 10 for the column test. For lysimeter 3 only results are obtained until L/S 0.5 and for lysimeter 5 results are obtained until L/S 1.5. So the results of lysimeter 5 could give a better impression of the results on the long term. The elements Mo, Cr and Se belong to this group.

c) The third group of elements shows a lower degree of leaching under field conditions for all lysimeters compared to the column test. The elements Ca, Fe, Mg, Ba, Cu and Sb belong to this group.
d) The fourth group of elements shows a higher degree of leaching under field conditions in both lysimeters compared to the column test. The elements Al, V, K and Na belong to this group. It is possible that on the long term the leaching of Al and V could be similar to the column test, but for Na and K the cumulative leaching is at the present L/S ratio already higher than at L/S=10 for the column test. For all these elements the leaching in lysimeter 3 is higher than in lysimeter 5.
e) Finally one element behaves different from all other elements: arsenic. In lysimeter 3 the leaching is higher and in lysimeter 5 the leaching is lower than found at the same L/S ratio at the column test.

For the other elements no judgement could be made because concentrations were below the detection limit, or were not measured in one of the cases. The heavy metals did not show any detectable leaching, because the pH is still too high (>10).

The leaching results under field conditions and under laboratory conditions are compared at the same L/S ratio. This means that the differences are not caused by differences in solubility. A difference between the various test conditions is the time scale. Most probably the observed differences are kinetically determined. More evaluation of the obtained data and more measurements at higher L/S ratio will probably give more insight in the mechanisms.

During three years Fruchter *et al.* studied the leaching behaviour of PFA in lysimeters in the USA [2]. Potential solubility-controlling solids were identified for Al, Ba, Ca, Cr, Cu, Fe, S, Si and Sr in the pore waters and leachate. From a laboratory test the authors concluded that equilibrium times between these nine elements and their solubility controlling solids were an order of days or less. These findings, except for Si, are not in agreement with our tentative conclusions.

Frigge has done similar experiments in Germany. The lysimeter was 2 m in height and results were reported after 44 months in operation [3]. The lysimeter results were compared to the German shake test (DIN 38 414 S4) and to the column test. In the paper not many details are given, only a graph of the sulphate leaching behaviour of bottom ash of a coal-fired power station. It appears that at a L/S ratio of 2 1 kg was leached at the lysimeter, 0.7 kg was leached in the shake test and 0.4 kg was leached at the column test. Besides the cumulative curves for the lysimeter and the column test were al L/S 2 already rather horizontal, while the curve of the shake test is still rising, giving a value of about 2 kg sulphate at a L/S ratio of 10. These results suggest that the column test gives to low figures for sulphate leaching with respect to the lysimeters. Unfortunately because we did not measured sulphate leaching in the column test, we are not able to compare these results with our results.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Utilization of wastes in ground improvement works

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A viable solution to waste disposal problem would be the reuse of wastes either by recycling or modify their properties to suit for various geotechnical applications. New cost effective technologies should be developed to provide a comprehensive solution to address the by-products disposal problem. In this paper, the various processing technologies involved in utilizing or treating wastes, and the product suitability for construction works have been discussed. Also the use of construction wastes such as excavated spoils and concrete debris for land reclamation and subsequent ground improvements have been proposed. The above methods serve as solution scenarios for various geo-environmental problems.

1.INTRODUCTION

The urbanization and rapid population growth has resulted in an enormous production of wastes. Several investigators reported the potential reuse of wastes such as wastewater sludges, dredged marine sediments, MSW fly ash and other non-conventional building and construction materials [1]. The properties of products derived from wastes related to their applications such as an admixture in stabilization of soft soil, non-conventional concrete aggregates, brick-making material, precast pavement blocks, and cement replacement material have been investigated. Research work in this field will include low temperature vitrification for aggregate, synthesis mineral stabilization, cement/concrete encapsulation application and metal recovery etc. The above category includes evaluation of municipal incineration fly ash as a blended cement material, development of sintered sludge as a construction material, recycling marine clay and industrial solid wastes into high value added civil engineering materials, and the development of adsorbents from municipal sewage sludge. Eventhough many technologies developed in handling wastes, a systematic approach of categorizing the wastes, their re-use and related environmental impact have not yet been properly brought out. Thus it is necessary to provide an awareness on the effective utilization of wastes, minimize the disposal cost, and thus creating a better living environment for our future. In this paper, the generation of wastes and their re-use potential for ground improvement applications has been briefly outlined.

2.RE-USE OF WASTES

The rapid industrial growth has resulted in the production of wide variety of wastes that impose severe environmental problems to the mankind. The dense population and industrial growth in the world results in the generation of huge wastes such as coal ash, iron and steel slag, sludge, concrete and rock powder, plastics and oil, but the limitation of space raise the disposal problem. The key role of Environmental Geotechnology has promoted geotechnical application of industrial wastes for the construction industry and waste management. Recently several attempts have been made towards the reuse of waste materials, thus reducing negative environmental impacts. The remediation projects using the ground improvement techniques are still in practice, and the research on the practical application of industrial wastes such as coal fly ash or steel slag containing pozzolanic compounds for improving the properties of clays has been well established. The use of fly ash as a structural material has received good attention in the world and this power generating industry by-product is economically attractive because of its usefulness to various engineering purposes such as embankment or caisson filler, road base material, man made island construction and liner material. The wastes containing fly ash or steel slag can also be used for the improvement of engineering and durability behaviour of dredged sediment [1] by properly treating them with cement based stabilizers such as carbonated aluminium salts (CAS). This successful utilization of wastes as a geo-material can decrease the treatment cost as well as reduce the pollution control. Hence there is a need to formulate solutions which take several geotechnical aspects to control and minimize environmental hazards, and to develop technologies and design procedures for geotechnical engineering works. The application of a by-product, formed as a result of burning industrial wastes with lime for improving the properties of a loam soil has been reported [2]. The utilization of industrial wastes for improving the properties of clays has high potential from Environmental Geotechnique point of view, and the new strategies for utilizing industrial wastes should be promoted comprehensively.

3.WASTE MANAGEMENT IN GEOTECHNICS

There is a thumb rule in waste management that waste minimization, reuse/recycling and energy recovery from wastes should preserve the natural resources, minimize the need of landfilling and protect the global environment. Treatment techniques such as volume reduction is recommended only if utilization solution is dropped. Also the waste treatment technologies should not involve high cost than disposal, and environmental impact has been given prime importance of waste disposal. The main important criteria for the use of wastes is that their physical and environmental properties of the residue should comply with the concerned specifications related to field application.

There is a need to classify and characterize the residues. But there are various policies and methods of handling wastes in different countries. The wastes can be mainly classified into hazardous and non-hazardous wastes (Figure 1). Radioactive wastes, and some chemical and biological wastes containing toxic substances which affect the humankind is classified under hazardous wastes. These hazardous wastes have less potential for its re-use and has to be properly disposed of in the controlled landfill sites. But the non-hazardous wastes can be further classified into construction wastes, industrial wastes, dredged wastes and other wastes. Under ***construction wastes***, waste bentonite, surplus excavated soil and demolished debris materials are the important items to be considered. In the past, these materials were treated as wastes and their disposal has been considered as a challenging task. In view of the rapid development in geoenvironmental engineering field, various methods have been developed to effectively utilize construction wastes as useful geo-materials. Figure 2 shows relationship between the treatment method and construction waste sludge application [3]. Sometimes crushing and screening equipments may be needed for specific engineering application while stabilization may be required to improve /modify the engineering behaviour of soils to suit the specifications. Demolition waste from construction sites has recently attracted due to its potential for utilization [4]. The reduction of strength as well as drying shrinkage has been tackled by adding sufficient quantity of pozzolanic materials such as fly ash, fully condensed silica flume. Since demolished debris properties can be comparable with limestone in road applications, the recycled aggregates can be used as lightweight materials to structures due to its high friction angle and low specific gravity. The pollution caused by secondary minerals due to the presence of salts such as chlorides and sulphates has to be examined [5]. However the use of minestones for embankments at roadways, railways, rivers, dams, land reclamation and backfilling has been recently increased. The poor engineering characteristics of construction sludges and heterogeneous nature of demolished debris can be improved by adding suitable pozzolanic materials such as cement, lime and fly ash.

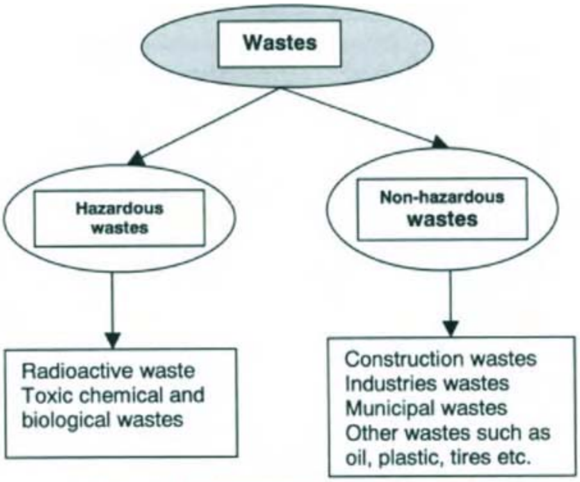

Figure 1. General classification of wastes

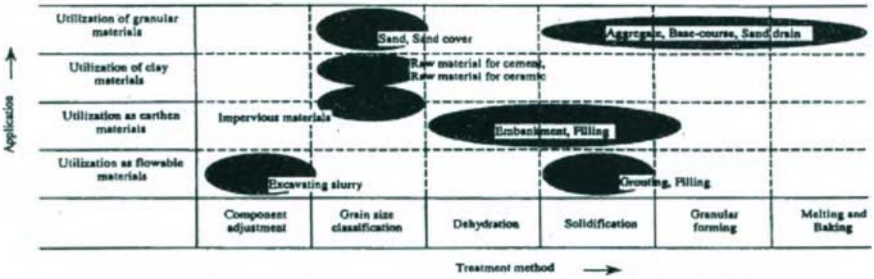

Figure 2. Relationship between treatment method and construction waste sludge application

There are several products that belong under ***industrial wastes*** category such as coal ash, municipal sewage ash, slag, plastic, tires, oil and other substances. Coal combustion results in the formation of three products such as bottom ash, fly ash and desulphurisation product. Out of the above products, fly ash has a high potential for utilization, and some of the applications include soil improvement, building material and foundations, subbase, land reclamation, embankments to form ash lagoons. Several investigators reported the successful application of Portland cement as one of the effective methods of treating industrial wastes in a solidification process. The generation of municipal sewage waste (MSW) residues is huge, and the ash product formed after burning of waste can be well utilized. This includes the utilization of bottom ash for land reclamation, wind and sound barriers, road sub-base, base for parking areas, aggregate substitute in Portland cement applications for marine reef, shore protection structures, final cover and grade materials at existing landfills requiring closure. By adding suitable hardening substances with concrete powder, it can be successfully used as subbase whereas rock powder has been wrapped into non-woven fabric bags and then used for seafloor improvement [6]. Waste oils, in general, can be used as fuels whereas high viscous oil can be used in stabilizing industrial waste and iron slags with stabilizers to obtain a final product of useable ground material [7]. But the above materials can be chipped into finer particles and then used with soil for filling or aggregate materials since they provide a certain amount of reinforcing effect. Water bodies such as river, lake and ocean require dredging for navigational purpose, and the ***dredged sediments*** should be disposed of. Recently several researchers established various applications of dredged sediments for beach nourishment construction aggregate, filling materials. Lime pile and lime injection techniques can be also used for improving the properties of contaminated marine clay [5]. An attempt has been made to convert the contaminated sediments and form a suitable commercial product such as porous pellets using sintering process [1]. The use of sintering process has demonstrated that dredged sediments can be suitably converted into pellets for decorative horticulture purposes. Hence lime treated contaminated marine clays and dredged sediments can be used for land reclamation, embankment construction or filling purposes.

4.ROLE OF SOIL MODIFICATION

Improving soil behaviour using standard modification methods such as compaction, preloading, electro-osmosis and grouting has emerged as a new technology. The selection criteria of ground improvement methods for different types of soils have been highlighted in Figure 3. Compaction has been proved successful to densify municipal solid waste, compacted clay liners and covers, and selection of appropriate compaction density and water content are important to achieve the required level in the field. Also the use of deep dynamic compaction (DDC) in landfill can stabilize wastes upto a depth of 12m, and this method is effective in reducing future settlements of closed landfills prior to construction. The use of extraction wells and drains to collect contaminated water and lower the ground water table to prevent contamination and hydraulic modifications especially in the waste containment systems. Soil vapor extraction (SVE) is another popular technique used to remove volatile organic compounds, and the by-products of anaerobic degradation of waste material such as carbon dioxide and methane can be removed to prevent migration of gases to avoid damage to landfill caps and liners. Ground fracturing is widely used to recover better extraction of oil and gas from wells. Thus hydraulic fracturing can used in rock and soil to increase the flow, and the above process can be achieved through a controlled blasting technique. Preloading and surcharge can be used to minimize the future settlement of landfills, and thus prevent crack or failure of landfill cover. Electro-osmosis can be used to extract contaminated water from soils whereas electrophoresis could be applied to concentrate, debater and consolidate waste slurries and sludges.

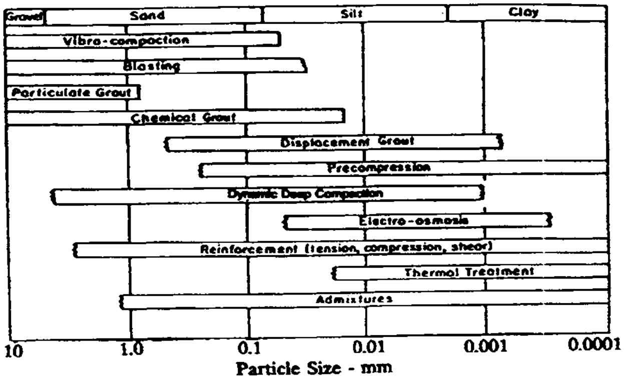

Figure 3. Selection criteria of ground improvement methods for soils.

In-situ remediation of soils can be achieved through compaction or penetration and jet grouting techniques. The formation of a grout curtain thus isolates waste material and prevent contamination of ground water due to leachates (Figure 4). Waste containment can be effectively achieved through deep chemical mixing, thermal or freezing and slurry walls. Also re-use of pozzolanic characterized wastes such as fly ash and lime can be used in the above techniques. However, long-term stability of chemical compounds should be evaluated before applying the above method in the field.

5.RISK ASSESSMENT OF WASTES

Even though wastes have potential of re-use in engineering applications, their impact on global environment, wastes-soil interaction and their stability on duration especially with changing environmental conditions should be carefully examined. The problems are related to mechanical stability as well as ground water and nearby water bodies contamination. The expected problems may be swelling of soil due to soil-wastes interaction due to the formation of ettringite [5]. The lateral migration of heavy metals and subsequent leaching process can affect the vegetation and contaminate the superficial soil. A risk assessment analysis should be carried out to predict the change in environment due to the use of wastes in ground improvement works. Hence the physico-chemical behaviour of waste materials result in the damage of structures due to polluting the nearby soil and aquifer. The main consideration should be emphasized by looking into possibility of long-term stability of wastes when subject to the adverse environmental conditions of pH, temperature, fluctuation of ground water table, acid rain and other chemicals attack. Also the engineering behaviour of the wastes should be carefully evaluated inview of low strength characteristics. Finally, the soil-contaminants interaction is the main phenomena to be studied when looking into the re-use of wastes in field.

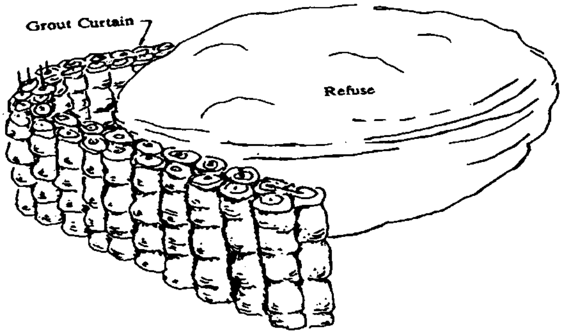

Figure 4. Waste isolation from ground water flow using grout curtain.

6.CONCLUDING REMARKS

The details of wastes generation and their re-use techniques especially in ground improvement works have been reported. It is suggested to evaluate the risk assessment before utilising wastes in ground improvement works. Based on the characteristics of wastes, and nature of re-use application of wastes in ground improvement works, the problem should be approached carefully. Predicted results on effective utilisation of various wastes and the formation of stable reaction products even under worst environmental scenarios should be considered. The use of waste light weight geo-material save large cost due to the reduction in the lateral earth pressure and the placement of stabilised fill against bridge abutments, retaining walls, sheet pile bulkheads, and below the grade building walls. The effective disposal of fly ash from the power plants can be solved by its re-use for various engineering applications.

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Leaching processes in cement-stabilised municipal incinerator air pollution control residues

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The geochemical and hydrological factors controlling field and laboratory leachate composition of cement stabilised air pollution control (APC) residues (41% APC residues, 22% cement, 3% Na_2CO_3, and 32% water, w/w) have been investigated. Field samples were taken as a function of hydrological conditions from a field lysimeter (3 x 5 x 1.5 m) containing cubic blocks (edge length, 0.5 m) during 3 rain events. It was assumed that the field leachate composition was probably not strongly influenced by diffusion processes because in the short time scale of the experiment (7 years), it was estimated that less than a millimeter of the block surfaces was leached. Laboratory experiments were carried out on ground samples at solid/liquid ratios of 0.05, 0.1 and 0.2 with an equilibration time of 28 days. The major components Ca, SO_4, Al and Si could be partially modelled by assuming calcium silicate hydrate (C-S-H), portlandite and ettringite to be the solubility controlling phases. There were obviously additional minerals that could not be taken into account in calculations because of the lack of data. Heavy metal concentrations were generally lower in the field leachate than in laboratory experiments and again could only be partially modelled. It is probable that cement minerals play an important role in their immobilisation. There are also indications that for some heavy metal anions, Ca metallates could be dominant solubility-limiting phases.

1. Introduction

The optimisation of laboratory leaching tests to predict the leaching behaviour in the field is an important aspect in waste management for the long-term protection of the environment, whether materials be landfilled or reused [1]. On the one hand it is necessary to understand present-day and on the other the long-term leachability; the latter being dependent on intrinsic properties of the waste material. Leaching tests try to cover both aspects, but are by necessity generally very much simplified. The comparability of laboratory and field leachates is based on the assumption that not only are the conditions (such as pH) and the processes that control contaminant mobility the same, but also the time frame of the leaching process. Where diffusion processes are important, time for equilibration is an important parameter. In this paper, we compare laboratory-leaching experiments with data from a field lysimeter containing cement-stabilised APC residues.

The use of cement to stabilise hazardous wastes is common practice and in Switzerland a significant proportion of APC residues from municipal solid waste incineration (MSWI) is

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stabilised with cement prior to landfilling. The APC residues are washed in order to remove salts, dried and mixed with cement in a ratio of approximately 2:1. Cement stabilisation of wastes reduces the contaminant mobility in two manners:

(1) The cement acts as a physical barrier to prevent leaching. The quality of the physical barrier directly depends on the strength of the resulting solid and can be optimised with a blending recipe.

(2) The cement matrix dominates leachate chemistry and thus affects contaminant mobility geochemically. In the case of APC residues heavy metals are the contaminants of interest. During hydration, heavy metal components can dissolve, adsorb to the matrix or be incorporated in the newly formed (cement) minerals, though there is still much to be learned about the binding mechanisms.

The aim of this paper is to illustrate and compare the dominant processes that control leachate composition in the laboratory and the field. The influence of hydrology on leachate chemistry will be illustrated. The concentration of leachate components will be explained in terms of dissolution/precipitation processes and discrepancies between field and laboratory data discussed.

2. Site

The field lysimeter was constructed in the winter 1990/91 next to the landfill Teuftal in Mühleberg, Switzerland (Fig. 1). It comprised two compartments containing cement-stabilised APC residues in the form of blocks and pellets [2, 3, 4]. The investigated lysimeter compartment contained blocks with an edge length of 0.5 m. They were prepared with 41% APC, 22% cement, 3% sodium carbonate, and 32% water (w/w). The lysimeter was approximately 1.5 m deep, had a surface area of 16 m^2, and was covered with geotextile, gravel (0.8 m) and humus (0.3 m) layers. It was dismantled in December 1997.

Fig. 1: The investigated field lysimeter during dismantling in December 1997

3. Methodology

Leachate discharge and composition was investigated as a function of hydrology during 3 rain events. Sampling and analysis are described in [3]. When dismantling the field lysimeter in December 1997, cores (10 cm diameter, 30 cm length) were taken from the blocks, packed in hermetically sealed plastic bags with soda lime to prevent CO_2 uptake and kept at –20°C until used in the laboratory leaching experiments. The material was then dried and ground to <0.25 mm. X-ray powder diffraction of the ground samples was performed with a Scintag XDS 2000 diffractometer (Cu-Kα-radiation). For the leaching experiments, 200 ml of suspensions (50, 100, 200 g L^{-1}) were prepared in triplicate in 250 ml polyethylene bottles. The samples were shaken for 27 days (equilibrium was reached during this time) and filtered through 0.45 μm nylon filters. The pH was measured directly after filtration using a combined glass electrode (Metrohm 6.0202.100) connected to a digital voltmeter (Metrohm 713). The electrode was calibrated by titrating 10 ml of a 0.01 M HCl solution with up to 6 ml 0.05 M NaOH using a dosimat (Metrohm 665). One part of each sample was then acidified with 1% (v/v) 65%-HNO_3 for analysis of cations. The filtrates were stored in 100 ml polyethylene bottles prior to analysis. All analysis of elements was performed in triplicate. Aluminium, Ca, K, and Na were measured by AAS (Perkin Elmer 5000 and for Al Varian Spectra-20). Chloride and SO_4 were determined using ion chromatography (Sykam) with a Sykam (AO4)

Table 1: Thermodynamic data used in calculations for I = 0 M and T = 25°C. Hydrolysis reactions are represented as $M^{2+} + H_2O \Leftrightarrow M(OH)^+ + H^+$.

		Aqueous species					Solids	
	Cations	OH	SO_4	Cl	CO_3	HCO_3		K_{SO}
Cu	MeX	-8.00[6]	2.36[6]	0.4[6]	6.73[6]	12.53[6]	$Cu(OH)_2$	8.68[7]
	MeX_2	-17.3[6]					CuO	7.65[7]
	MeX_3	-27.8[6]						
	MeX_4	-39.6[6]						
Ni	MeX	-9.86[6]	2.29[6]	0.72[6]	4.83[8]	12.55[8]	$Ni(OH)_2$	10.80[9]
	MeX_2	-19.0[6]	3.20[6]				Ni_2SiO_4	14.54[10]
	MeX_3	-30.0[6]						
	MeX_4	-44.0[6]						
	Anions	H	Ca					
Mo	MeO_4X	4.23[11]	2.57[11]				$CaMoO_4$	-8.51[11]
	MeO_4X_2	8.23[11]						
W	MeO_4X	3.5[9]					$WMoO_4$	-9.46[10]
	MeO_4X_2	8.1[9]						
	Cement minerals							
	$Ca_6Al_2O_6(SO_4)_3.32H_2O$						Ettringite	57.45[12]
	CaH_2SiO_4						}C-S-H{	14.98[13]
	$Ca(OH)_2$							20.80[13]

column. Silicon was measured spectrophotometrically with the molybdenum blue method using a flow-injection analyser (FIA, Ismatec ASIA). Copper, Mo, Ni, and W were measured by ICP-MS (Elan 5000A, Perkin Elmer) using the standard addition method in order to prevent matrix effects.

All handling of the sampling material in the laboratory was undertaken in a CO_2-free atmosphere. Water was taken from a 17MΩ ultrapure system (Barnstead Nanopure), with a 0.2-μm in-line filter. Before use, the ultrapure water was boiled and cooled to 20 °C under Argon. Polyethylene bottles were leached with acid (~0.6 M diluted from concentrated HNO_3) for at least 24 hours and rinsed with ultrapure water.

Thermodynamic calculations were performed with the aid of the computer program MQV40TIT [5]. The solubility and stability constants used for the calculations are given by [3] and in Table 1. They were adjusted for the ionic strength of the solutions after the Davies equation.

4. Results and discussion

The leachate is of almost constant composition (to within a factor of 2-3) between rain events and is diluted during rain events [3]. This applies to heavy metal concentrations as well as to the major components. An example of the characteristic changes in leachate composition in response to a rain event is shown in Fig. 2. An increase in discharge appears to be accompanied by a dilution of major and minor leachate constituents, represented in Fig. 2 by the electrical conductivity and by Zn concentration. Most heavy metal concentrations correlate directly to the electrical conductivity of the leachate. The leachate dilution following a rain event appears to be the consequence of preferential flow. A portion of the rainwater appears to pass through the landfill body with little interaction with the landfilled material while the rest passes through more slowly. Assuming a travel distance corresponding to the depth of 1.5 m, and a residence time of approximately 4 days, the water can be assumed to be passing through the sandy fill between the blocks at a rate of roughly 1×10^{-6} m s^{-1}, which is not an unreasonable value.

Estimates of the total leached quantities of major and minor components indicate that, under the assumption that all surfaces are available for leaching, significantly less than 0.1 mm of the block surfaces has been leached within the first 6 years. With such a short diffusion length, diffusion processes probably do not control leachate composition. It is plausible that the leachate composition is in quasi equilibrium with the minerals of the cement-stabilised APC residue blocks.

The XRD spectrum (Fig. 3) of the cement stabilised APC shows an increased background in the region from 28 to 38° 2θ. This is typical for amorphous calcium silicate hydrate gel (C-S-H). C-S-H is the main constituent of hydrated Portland cements. It may contribute to over 60% (w/w) of a cement [14]. The XRD peaks could be attributed to ettringite ($Ca_6Al_2O_6(SO_4)_3 \cdot 32H_2O$), portlandite ($Ca(OH)_2$), quartz ($SiO_2$), calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), and a calcium aluminium oxide hydrate of the composition $Ca_3Al_2O_6 \cdot XH_2O$. All of these minerals are common cement minerals. The dominant presence of ettringite in the sample is in contrast to normal Portland cement pastes. In these, ettringite does not usually persist, but dissolves, followed by the precipitation of monosulfate ($Ca_4Al_2O_6(SO_4) \cdot 12H_2O$) [14]. However, monosulfate could not be detected in the XRD spectrum, indicating that there has been little or no transformation of ettringite into monosulfate. Possible reasons for a stable ettringite phase are a high SO_4/Al ratio in the paste or the contact with carbonate, which reacts with monosulfate in the presence of $Ca(OH)_2$ to produce ettringite and hemicarbonate ($Ca_4Al_2O_6(CO_3)_{0.5} \cdot 12H_2O$). Compared to Portland cement, the investigated APC residues do

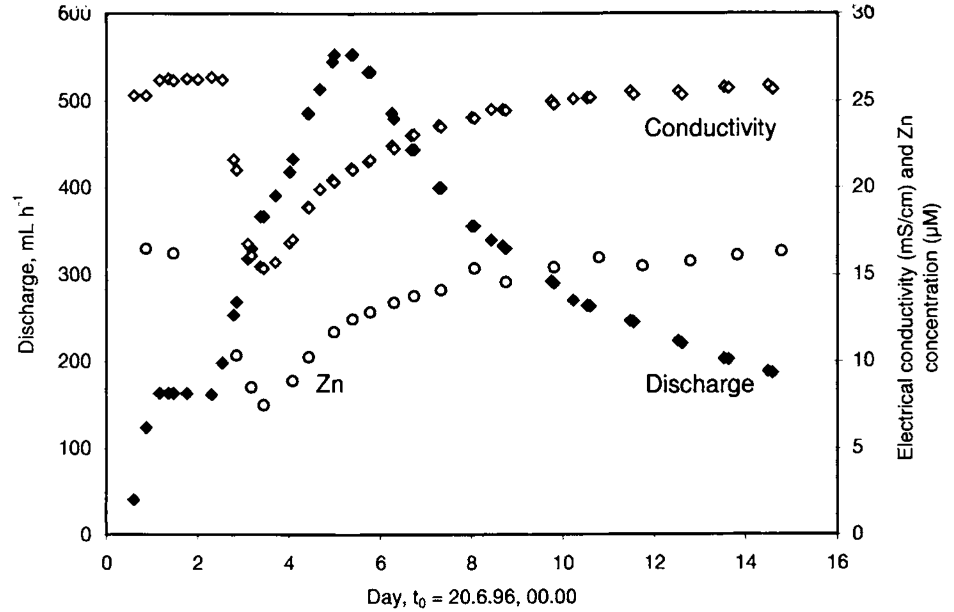

Fig. 2: Discharge (◆), electrical conductivity (◇) and Zn (o) concentrations in lysimeter leachate as a function of time after a rain event.

not have a higher SO_4/Al ratio. The presence of calcite may be a product of the reaction of Na_2CO_3 with the cement matrix but there has probably also been some contact with atmospheric CO_2 at some stage. It is not clear, what mineral caused the peak at a 2θ of 11°. Hemicarbonate, Friedel's salt ($Ca_4Al_2O_6Cl_2 \cdot 10H_2O$, an AFm phase) and hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$) have peaks close to 11° and their presence in a cementitous matrix is plausible [14].

In the laboratory leachates the concentrations of the major components of unlimited solubility, OH, Na, and Cl increase with the solid/liquid ratio (Fig. 4). This trend continues for the field leachates, where the solid/liquid ratio is expected to be high. The results imply a solid/liquid ratio in the field of around 500 g L^{-1}, which means, that during percolation one litre of leachate stays in chemical equilibrium with 500 g of the solid matrix. This would be equivalent to a leaching thickness in the order of 1 to 2 mm.

Dissolution/precipitation processes appear to control the solubility of the major components Al, Ca, Si and SO_4. Thermodynamic modelling of the field and laboratory data has been performed in order to find possible solubility controlling phases. Because C-S-H is the main constituent of hydrated Portland cements, it has to be taken into account. C-S-H forms solid solutions between the approximate limits $0.85<Ca/Si<1.70$ (mole ratio). Its dissolution proceeds incongruently with aqueous Ca concentrations being much greater than those of Si. In addition, the solubility of C-S-H is dependent on the Ca/Si ratio of the solid phase. These factors make it difficult to model the C-S-H dissolution. Berner [13] proposed a dissolution model assuming that the C-S-H system is represented by a nonideal mixture of the congruently soluble components SiO_2, CaH_2SiO_4 and $Ca(OH)_2$ (portions depending on the Ca/Si ratio). This model was used in the thermodynamic calculations.

Because the Ca/Si ratios of the C-S-H phase were not known, the dissolution model was

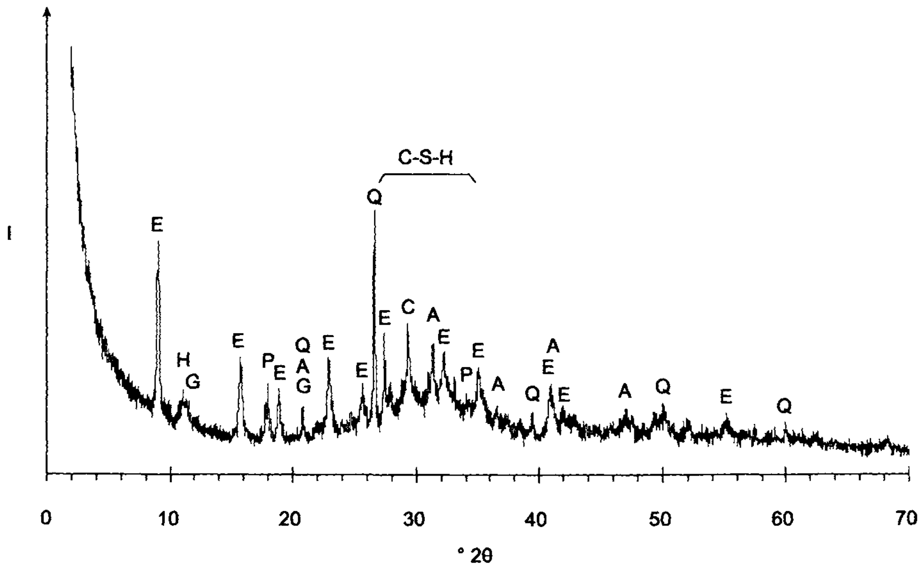

Fig. 3: XRD spectrum from cement stabilised APC (CuK$_\alpha$ radiation). E – ettringite; H – hemicarbonate, Friedel's salt or hydrotalcite; G – gypsum; P – portlandite; Q – quartz; A – calcium aluminium oxide hydrate; C-S-H – amorphous calcium silicate hydrate; C – calcite.

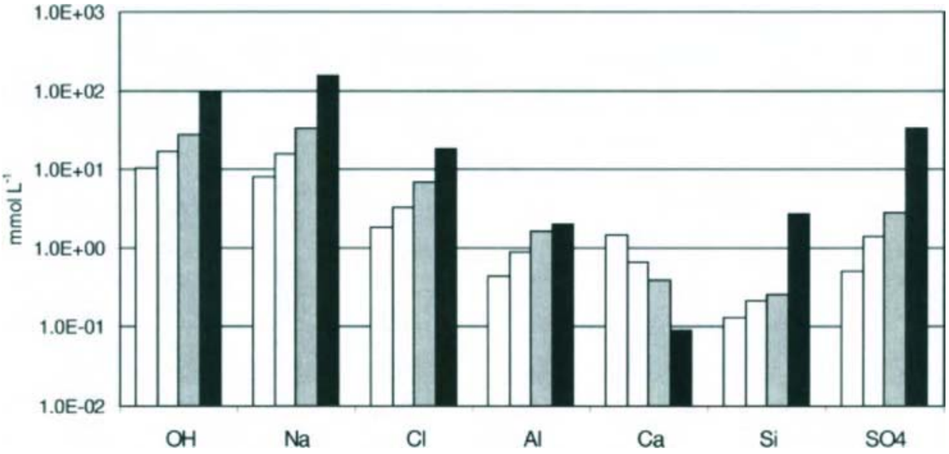

Fig. 4: Concentration of major components in the leachate of the 50, 100, 200 g L^{-1} suspensions (three bars on the left), and of the landfill (black bars on the right).

XRD spectrum (ettringite, portlandite, quartz, and calcite) and other known cement minerals (hydrogarnet, hydrated gehlenite, and gypsum) were tested as solubility controlling phases. The measured Ca concentrations in the field and in the laboratory could be well modelled by C-S-H, assuming a Ca/Si ratio of 1, which takes portlandite into account as well (Fig. 5). The C-S-H model overestimates the Si concentrations, though, by 1 order of magnitude. It has been pointed out before, that the Berner dissolution model overestimates Si levels in alkali bearing solutions by 1-2 orders of magnitude [15] and this may provide an explanation for our system. Ettringite seems to control Al and SO_4 solubility in the laboratory. But in the field, the Al concentrations are much lower than would be expected in equilibrium with ettringite. Of the plausible Al containing minerals with known solubility constants, none is less soluble at a pH of 13. It is probable that a calcium aluminium (silicon) oxide hydrate plays an important role in controlling Al solubility.

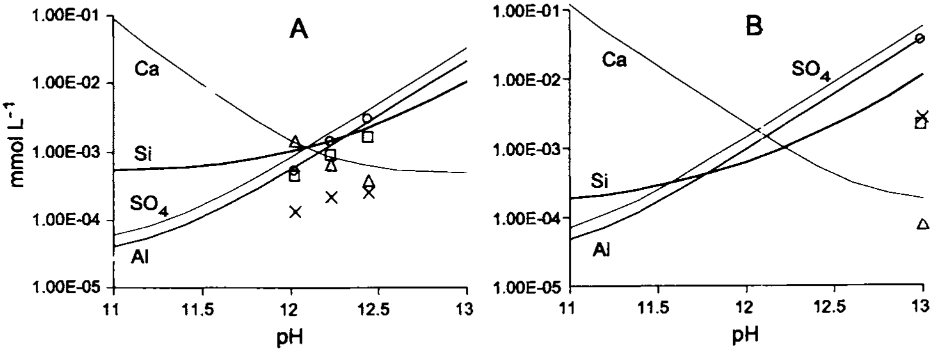

Fig. 5: Calculated pH dependent solubility curves (lines) for C-S-H, portlandite and ettringite. Lines represent the concentrations of Al, Ca, Si and SO4 compared to measured concentrations (symbols). A: Laboratory data, solubility constants were corrected to an ionic strength of I=0.03. B: Field data, solubility constants were adapted to an ionic strength of I=0.15. Symbols: □ - Al, △ - Ca, X - Si, O - SO4.

Of the minor components, Cu and Ni have been chosen to represent cations and Mo and W the anions. For the latter two components, solubilities and concentrations appear to correlate to the solid/liquid ratio in the laboratory experiments, whilst having lower concentrations in field samples (Fig. 6). The dissolved concentrations of Cu and Ni appear to be independent of the solid/liquid ratio. Of the four trace elements, only Ni can be modelled in the laboratory as well as in the field. Ni-silicate may control Ni solubility. However, little is known about heavy metal silicates and their importance in cementitous systems.

Mo and W share the advantage that their laboratory data can be well modelled with Ca-metallates. In the field, the models that fit the laboratory results overestimate Mo and W solubility. On the one hand, this could suggest that the trace elements in the field are not in chemical equilibrium with the leachate and that diffusion is important. On the other hand, it is possible that the trace elements are bound into the cement matrix in a metastable phase that undergoes diagenesis in laboratory equilibration experiments. This may by caused by the difference in pH, which can affect the affinity of heavy metals for different phases.

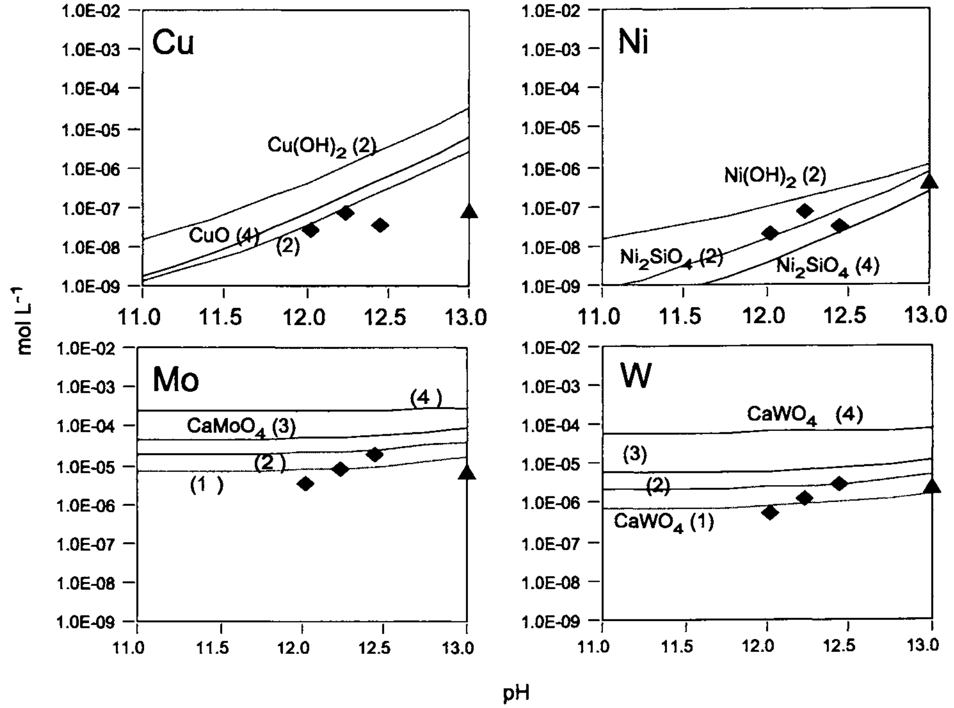

Fig. 6: Calculated pH dependent solubility curves (lines) for Cu, Ni, Mo and W compared to measured concentrations (symbols: ◆ laboratory, ▲ field). Curves are adapted to calculated ionic strength (I) and measured Si or Ca concentrations, respectively. (1) I=0.015, Si=0.133 and Ca=1.43 mmol L^{-1}, (2) I=0.03, Si=0.217 and Ca=0.668 mmol L^{-1} (3) I=0.06, Si=0.257 and Ca=0.383 mmol L^{-1} (4) I=0.15, Si=2.7 and Ca=0.09 mmol L^{-1}.

The role of cement in the immobilisation of heavy metals is not fully understood and to date there is not sufficient information to determine whether or which cement minerals play a role in controlling the solubility of the different heavy metals. However, there is evidence to suggest that C-S-H can incorporate metals such as Zn [16] thereby lowering their solubility. This is also likely to be the case for other metals and cement minerals.

5. Conclusions

The field leachate composition was probably not strongly influenced by diffusion processes because of the limited time scale of the experiment (7 years). The laboratory and field leachate composition should thus have been comparable because both could be controlled by a quasi-thermodynamic equilibrium between the solid phase and the leachate. This was only found to be partially true. Though the solubility of the major components Ca, SO_4, Al and Si can be modelled using C-S-H, ettringite and portlandite as the solubility limiting phases in the laboratory and the field data, there are obviously additional minerals that should be taken into account. However, the thermodynamic database is limited. Most heavy metal concentrations are lower in the field leachate than in laboratory experiments and it is probable that cement minerals play an important role. Here again a lack of knowledge of the processes involved prevents us from extrapolating from the laboratory to the field. However, it should be pointed out that the difference between laboratory and field data is usually less than one order of magnitude. Also there are indications that for anions, Ca metallates could be dominant solubility-limiting phases. Such comparisons allow us to pinpoint areas in which further information is required.

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USING RICE HUSK ASH AS A CEMENT REPLACEMENT MATERIAL IN CONCRETE

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Many countries have the problem of shortage of conventional cementing materials. Recently there are considerable efforts worldwide of utilizing indigenous and waste materials in concrete. One of such materials is the rice husk which under controlled burning, and if sufficiently ground, the ash that is produced can be used as a cement replacement material in concrete. This research has been undertaken to study the main characteristics of the Rice Husk Ash (RHA), properties of fresh concrete and development of the fundamental properties of hardened concrete. Also, the research involves developing a comprehensive engineering data-base on RHA concretes including durability aspects such as long term performance in artificial sea water (5% NaCl solution). The chloride ions permeability and chloride diffusion coefficient were measured using potentiometric titration analysis. Moreover, the porosity and pore structure of concrete were performed using Mercury Intrusion Porosimetry (MIP). The obtained test results showed that using RHA improved the different studied properties of concrete. In this paper, experimental program, test results and analysis as well as conclusions are presented.

1. INTRODUCTION

Recently housing construction with local raw materials has received research attention in developing countries. Pozzolanic materials of plant and artificial origins and natural occurring pozzolans have been of much concern in Africa and Asia [1]. During growth, some plants absorb silica from the soil and assimilate it into their structures; one such plant, with a high concentration of silica, is the rice plant [2]. Rice husk has been reported to constitute about 20% by weight of ash when incinerated; the resultant ash contains 90-96% silica [3]. Also, Mehta [4] has reported that its high ash and lignin contents (20-30% lignin) make it unsuitable as raw material for paper manufacturing. Apart from limited uses as a source of heat in some rice mills, the bulk is burned in open heaps in order to dispose it.

The high ash and lignin present in the husks make them unsuitable economic material for cellulose production. A convenient method of getting rid of rice husks is by burning them in open fields or as fuel for steam generators. The burning operation produces large quantities of ash, about 20% by weight of husks. This consists essentially of silica which is in a relatively inert form and is thus not useful either for agricultural or industrial purposes [5].

Rice husk ash concrete is very much like fly ash/slag concrete with regard to strength development. The important exception is that rice husk ash is a very active pozzolanic material, and the results of the pozzolanic reactions are evident at early ages rather than later as is the case with other replacement cementing materials [6]. Replacing by even small amount of RHA is beneficial to the strength development of concrete. This suits well with the present understanding in concrete technology, whereby most current national specification allows the addition of minor constituents to cement. Strength reductions are fairly obvious at higher replacement levels; this is somewhat expected as the water to cementitious material ratios of these mixes are rather high [7].

Chloride ions may enter easily into fresh concrete from the mix components, such as cement, aggregate, mixing water and chemical admixtures, or from chloride contaminates. The chloride ions may penetrate into hardened concrete from external sources, such as curing water, deicing salts, salt spray and sea water. Chloride ions may be present in concrete in several states [8] : (a) strongly bound by tricalcium aluminate hydrates (and to a lesser extent by tetracalcium alumino-ferrite hydrates) mainly in the form of calcium chloroaluminate, (b) loosely bound (immobilised by calcium silicate hydrates), and (c) free in solution (water-soluble) in the pore space. Migration of chloride ions occurs primarily through diffusion processes. The arbitrary limits of diffusion coefficient fall in the range of 10^{-7} and 10^{-8} cm^2/sec [9].

It is well known that the rate of chloride ion diffusion into concrete is related to the permeability and pore size distribution. Concretes made with blended cements generally have lower permeability and more discontinuous pore structure than plain portland cement concrete. Therefore, the diffusivity of chloride ions in blended cement concretes tends to be lower [10]. Therefore, the pore structure of concrete, perhaps more than any other characteristic of the materials, affects the behavior of the concrete [11].

2. MAIN CHARACTERISTICS OF RICE HUSK ASH

The rice husk ash is abbreviated here as RHA_{10} and RHA_{60}. 10 and 60 in the subscript indicate the grinding time in minutes. The colour of RHA is white. The specific gravity of ash (2.25) is about two-thirds the specific gravity value of ordinary portland cement (3.16). The fineness (specific surface area) of RHA varies slightly depending on the period of grinding. The relationship between fineness and particle size of RHA with the grinding time is indicated in Figure 1. The effect of increasing the grinding time on the particle size and shape of particle size ditribution profiles of RHA_{10} and RHA_{60} are shown in Figure 2. Determination of these properties was undertaken at the facilities of Osaka Cement Company according to the specifications provided by Japanese Industrial Standard (JIS).

The chemical composition of the RHA indicates that the combined proportion of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), and iron oxide (Fe_2O_3) in the RHA_{10} and RHA_{60} ash was 93.25%. This satisfies the ASTM C618-78 [12] requirement for chemical composition which stipulates a minimum combined proportion of 70%. The carbon content of the RHA_{10} and RHA_{60} ash determined as loss on ignition, was 3.3%. This also satisfies the ASTM requirement for loss on ignition which should not exceed 12%.

The pozzolanic activity of RHA was examined by the method based on variation in electric conductivity of RHA in a saturated $Ca(OH)_2$ solution [13]. According to Sugita et al [14], the pozzolanic activity can be estimated using the variation in electric conductivity. The results of variation in electric conductivity of RHA_{10} and RHA_{60} are 0.7 mS/cm and 0.9 mS/cm, respectively and RHA_{10} and RHA_{60} fall within the range of variable pozzolanic.

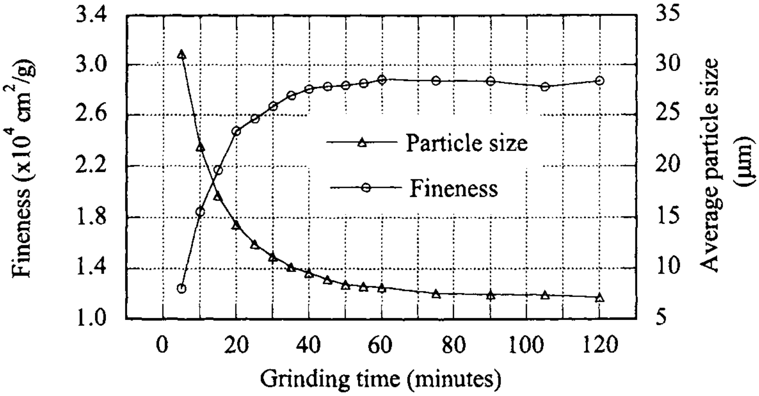


Figure 1. Particle size and fineness of RHA vs. grinding time.

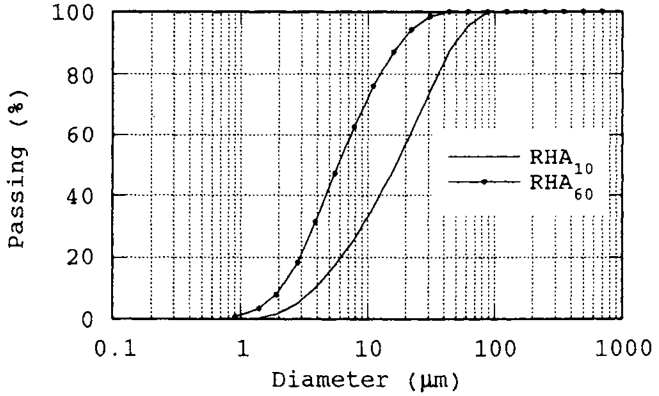


Figure 2. Particle size distribution of RHA_{10} and RHA_{60}.

The initial and final setting times of Ordinary Portland Cement (OPC) with RHA pastes are shown in Table 1. It is concluded that the water-cement ratio increases with the increasing of the RHA content and water-cement ratios of RHA_{10} are larger than those of RHA_{60}. The initial and final setting times of RHA_{10} pastes increase with increasing of the replacement percent but the initial setting time of RHA_{60} pastes decreases when the replacement percent increases.

Table 1

Initial and final setting time of OPC with RHA.

Cement OPC : RHA	W/(OPC+RHA) ratio	RHA type	Setting time (hour-minute) Initial	Final
100 : 0	0.280		2-25	3-22
90 : 10	0.364		2-31	3-49
80 : 20	0.444	RHA_{10}	3-03	4-28
70 : 30	0.525		3-02	5-17
60 : 40	0.608		3-10	5-40
100 : 0	0.280		2-25	3-22
90 : 10	0.308		2-09	3-18
80 : 20	0.353	RHA_{60}	1-55	3-39
70 : 30	0.399		1-29	4-17
60 : 40	0.448		1-24	4-20

Table 2

Mix proportions details of studied RHA_{10} concrete mixtures.

Mix No.	1	2	3
Replacement, percent	0	10	20
OPC, kg/m^3	350	315	280
RHA_{10}, kg/m^3	0	35	70
Water, litre/m^3	210	210	210
Sand, kg/m^3	844	870	865
Gravel, kg/m^3	854	881	875
Sand/total aggregate, ratio	0.50	0.50	0.50
Water/(OPC + RHA), ratio	0.60	0.60	0.60

On the other hand, the final setting time of RHA_{60} pastes increases with the increase in the replacement percent. The results indicated that the setting times were still within the recommended range for ordinary portland cement (OPC) paste [15]. Also, The results agree with the findings of Cook et al [16] who reported increases in setting times of RHA pastes over those of plain cement paste.

3. EXPERIMENTAL WORK

Three concrete mixtures with RHA_{10} only were studied. The OPC was replaced with 0%, 10%, and 20% of RHA_{10}. The mix proportions details of concrete mixtures are summarized in Table 2. The materials that have been involved in the experimental work were selected from local sources in Japan. The properties of used OPC comply with (JIS) specifications. The used sand has 2.58 specific gravity, 2.76 fineness modulus and 1.37 % water effective absorption. The coarse aggregate is crushed basalt has 2.61 specific gravity, 15 mm nominal maximum size, and 6.9 fineness modulus.

The measured parameters represent : (a) properties of fresh concrete such as slump, air content, and unit weight, (b) properties of hardened concrete such as compressive strength, tensile strength, flexural strength, static Young's modulus, horizontal and vertical dynamic Young's modulus, Poisson's ratio, pulse velocity, (c) chloride ion permeability, which includes total and soluble chloride contents as well as the diffusion coefficient, and (d) pore structure, which include cumulative pore volume, total porosity, pore size and its distribution as well as total pore surface area. The procedures, equipment, and apparatus used are described in details in [17].

4. FUNDAMENTAL PROPERTIES OF RHA CONCRETE

The properties of fresh concrete are included in Table 3. Furthermore, Table 4 shows the properties of RHA concrete cured in water until testing. While Table 5 gives the properties of RHA concrete cured 7 days in water and put in curing room conditions with temperature degree of 20°C and 80% relative humidity until testing.

Data of Table 3 show that : (a) the concrete slump decreases with increasing the replacement percent of RHA due to large specific surface area of RHA, (b) the air content of RHA concrete increases with increasing RHA content due to the difference between the finesses of OPC and RHA, and (c) the unit weight of concrete decreases with increasing the replacement percent of RHA due to the change in the specific gravity of both OPC and RHA.

Tables 4 and 5 indicate that with increasing RHA content the compressive strength decreases up to 28 days. After that, RHA concrete shows the same or higher strength than those of control mix. Further increase in the RHA content retards the strength development largely due to the higher water demand for these mixes. Hilmi Bin Mahmud [7] has studied the development of RHA concrete strength with high replacement percents and his findings confirmed the results of present study. In the second type of curing, the RHA concrete strength shows about 85% in compressive of that cured in water.

The development rate of tensile strength with time is slightly low for the first 7 days, after that, almost all mixes have the same rate of the tensile strength development. The difference between the tensile strength of concrete of the two types of curing is found to be not more than 5%. The increasing of RHA content does not affect the values of tensile strength especially after 28 days. Flexural strength results show approximately similar trend as that of the tensile strength. The results show that no change in the value of flexural strength takes place except at 180 days due to increasing the content of RHA from 10% to 20%. Also, from the results of Table 5, it can be concluded that the inclusion of RHA in concrete does not significantly affect the static modulus of elasticity. The obtained data of specimens cured in the second curing type confirmed with the work reported in Ref. [18].

The horizontal dynamic Young's modulus (E_h) decreases as the RHA content increases at the early age of concrete. After that, RHA concretes show slightly higher values of (E_h) than those of OPC mix. The long term results of (E_h) showed that the static and dynamic moduli of elasticity of RHA concrete did not affect. The second curing method shows lower values of E_h than those of water curing.

Table 3

Properties of fresh concrete of RHA.

Mix No.	1	2	3
Unit weight (t/m^3)	2.324	2.292	2.244
Slump, (cm)	14.40	11.10	5.40
Air content	1.70	1.80	2.25

Table 4

Properties of RHA hardened concrete (water curing).

Mix	Property		1-day	3-day	7-day	28-day	90-day	180-day
1	Strength (kg/cm^2)	Compressive	36	130	213	317	341	402
		Tensile	5.4	20.5	29	32	39	40
		Flexural	12	32	41	49	59	63
	Young's Modulus (x10^5 kg/cm^2)	Static	0.92	1.9	2.5	2.96	3.18	3.42
		Dynamic (E_h)	1.38	2.45	3.25	3.47	3.49	3.93
		Dynamic (E_v)	1.39	2.54	3.28	3.54	3.82	4.02
	Poisson's ratio		0.152	0.178	0.198	0.217	0.217	0.214
	Pulse velocity (km/sec)		1.54	2.20	2.37	2.46	4.41	4.45
2	Strength (kg/cm^2)	Compressive	28	107	174	251	312	428
		Tensile	4.4	16.6	23.1	28.4	38	39
		Flexural	10.6	30.4	40.8	45	55	58
	Young's Modulus (x10^5 kg/cm^2)	Static	0.44	1.87	2.29	3.22	3.29	3.53
		Dynamic (E_h)	0.81	2.34	2.89	3.53	3.43	3.76
		Dynamic (E_v)	0.80	2.40	2.91	3.66	3.61	3.99
	Poisson's ratio		0.16	0.173	0.180	0.22	0.188	0.212
	Pulse velocity (km/sec)		2.30	3.64	2.31	4.29	4.37	4.44
3	Strength (kg/cm^2)	Compressive	24	80	177	209	275	377
		Tensile	2.7	13.5	22.5	35.0	37.9	39.42
		Flexural	9.7	28.5	41	45	54.5	65.2
	Young's Modulus (x10^5 kg/cm^2)	Static	0.62	1.63	1.96	2.95	2.48	3.40
		Dynamic (E_h)	0.85	2.15	2.74	3.62	3.87	3.94
		Dynamic (E_v)	0.88	2.18	2.79	3.64	3.93	4.02
	Poisson's ratio		0.149	0.156	0.180	0.211	0.192	0.215
	Pulse velocity (km/sec)		2.46	3.6	3.94	4.37	4.46	4.50

Table 5

Properties of RHA hardened concrete (7 days water curing and 20°C + 80% RH till testing).

Mix	Property		28-days	90-days	180-days
1	Strength (kg/cm^2)	Compressive	312	326	368
		Tensile	33.3	35.7	38
		Flexural	47.7	57.5	80
	Young's Modulus (x10^5 kg/cm^2)	Static	2.86	2.88	2.70
		Dynamic (E_h)	3.45	3.48	3.56
		Dynamic (E_v)	3.50	3.65	3.80
	Poisson's ratio		0.199	0.173	0.172
	Pulse velocity (km/sec)		2.22	3.34	4.17
2	Strength (kg/cm^2)	Compressive	239	261	351
		Tensile	27.6	32.1	34.7
		Flexural	39.1	46.2	61.4
	Young's Modulus (x10^5 kg/cm^2)	Static	2.98	2.55	2.22
		Dynamic (E_h)	3.29	3.42	3.07
		Dynamic (E_v)	3.32	3.15	3.42
	Poisson's ratio		0.181	0.189	0.157
	Pulse velocity (km/sec)		4.16	4..27	4.27
3	Strength (kg/cm^2)	Compressive	216	247	320
		Tensile	29.3	31.69	34.52
		Flexural	31.1	45.4	59.1
	Young's Modulus (x10^5 kg/cm^2)	Static	2.68	2.27	1.95
		Dynamic (E_h)	298	3.09	3.10
		Dynamic (E_v)	3.22	3.42	3.36
	Poisson's ratio		0.185	0.166	0.194
	Pulse velocity (km/sec)		4.08	4.15	4.17

The OPC mix gives higher E_h than the values of RHA concrete. After 7 days, with the second curing method there was no difference in the vertical dynamic Young's modulus (E_v) due to increasing the content of RHA from 10% to 20 %. The concretes cured in water show higher values of E_v than those of the second curing method.

RHA concretes show slightly lower Poisson's ratio than those of the OPC mix at early ages in the case of water curing. At long term ages of water curing, all mixes give approximately the same Poisson's ratios and OPC mix shows higher Poisson's ratio than those of the RHA mixes. RHA concrete with the second curing method shows different values of Poisson's ratios with progress in time and all values are lower than those of water curing. Further, the values of pules velocity of concrete cured in water are higher than those of the second curing method. The obtained results of pulse velocity conflict with the finding of Ikpong [19], in his work, the pulse velocity decreases with increasing RHA replacement percent but in tthe present research, the pulse velocity fairly increases with increasing RHA content until 20%. The RHA concrete give higher pulse velocity than those of the OPC mix.

5. PERMEABILITY AND CHLORIDE DIFFUSION IN RHA CONCRETE

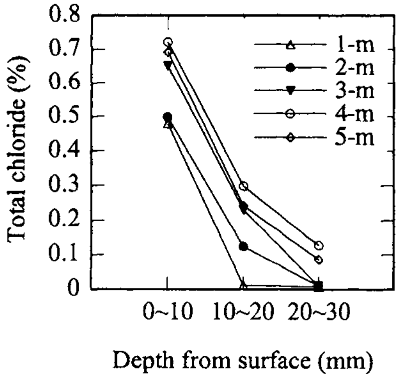
Chloride in concrete is an important factor contributing to concrete deterioration. The chlorides may be considered to be present either in a bound or a free condition. It is the free chloride levels in structural concrete that promote corrosion of the reinforcement. However, most existing specifications restricting the chloride content of concrete are based on total chloride levels. Thus it is important to understand the relationship between free and total chloride content. Sangha [20] stated that chloride threshold limits should eventually be expressed in terms of free chloride content. Marusin [21] mentioned that the corrosion threshold limit for soluble chloride ion concentrations in normal weight reinforced concrete is about 0.03 percent by concrete weight.

The total chloride content is generally obtained by removing the chloride from a sample by titration analysis (using nitric acid). On the other hand, the water soluble chloride content is determined by immersion of the sample in hot water, also using titration analysis. Furthermore, from the obtained results listed in Table 6, the distribution of chloride concentrations at different depths of cover were plotted in Figure 3 and Figure 4 to obtain the chloride concentrations profiles .

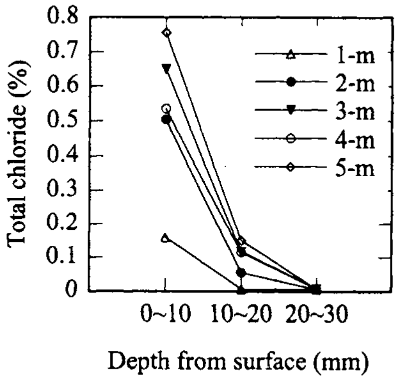
The ability of RHA mixtures to reduce the potential detrimental effects of chloride intrusion into concrete is made clear from the results obtained, where, concretes containing RHA outperform the specimen containing OPC alone. The levels of total and soluble chloride ions of Table 6 show large reductions as the depth of concrete zones surveyed increased as shown in Figure 3 and Figure 4. For concretes studied, the first 10 mm of concrete cover provides little barrier to chloride ion penetration and underscores the importance of concrete cover to the reinforcement. On the other hand, all the results of zone 20~30 mm show lower values of total chloride ions content than the limits of reinforcement corrosion threshold.

From the data of Table 6, it is evident that there are significant reductions in chloride ions permeability due to replacing the OPC with RHA. As the replacement level of the RHA increases from 10% to 20% by weight the results were affected and low chloride ions contents were obtained. Consequently, concrete containing RHA may require less depth of cover to protect the reinforcing steel than those concretes using OPC alone. The obtained results of soluble chloride ions contents of zone (20~30 mm) for RHA concretes are smaller than the limits of threshold for corrosion of steel.

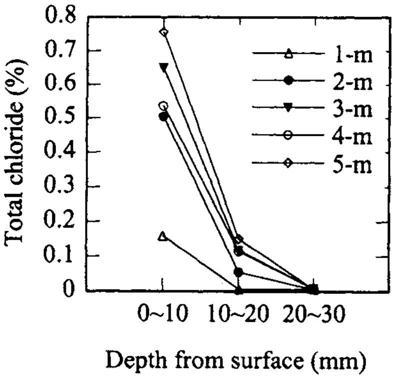
Gaynor [22] reported that one-half or three-fourths of penetrated chlorides ions in hardened concrete are soluble in water and free to contribute to corrosion, but RHA concrete mixes show lower percent than that reported by Gaynor. In the present research, RHA concretes show lower ratio of soluble/total chloride ions content than those of OPC concretes.



(a) Mix No. 1

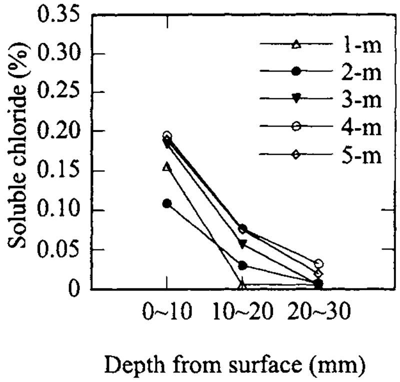


(b) Mix No. 2

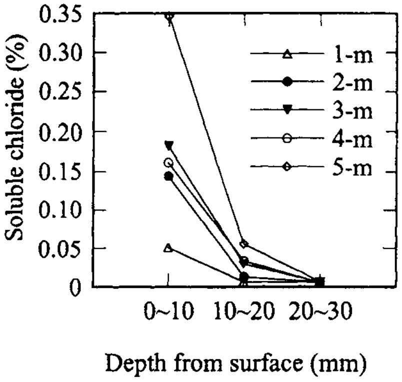


(c) Mix No. 3

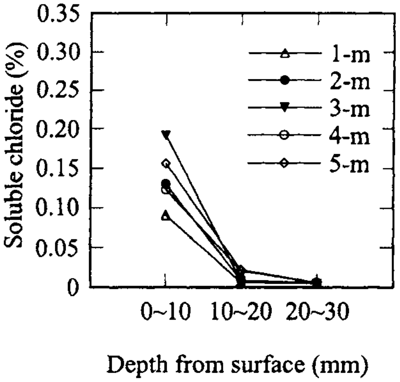
Figure 3. Total chloride content profiles.



(a) Mix No. 1



(b) Mix No. 2



(c) Mix No. 3

Figure 4. Soluble chloride content profiles.

Table 6

Results of total and soluble chloride ions as percent by weight of concrete.

Mix	Chloride	Depth	Exposure period to 5% NaCl solution (month)				
No.	type	(mm)	1	2	3	4	5
1	Total	0~10	0.47998	0.49890	0.65234	0.7218	0.69219
		10~20	0.01212	0.12410	0.22993	0.29789	0.24204
		20~30	0.00740	0.01107	0.01107	0.12708	0.08625
2		0~10	0.15910	0.50508	0.6499	0.53628	0.75589
		10~20	0.00690	0.05515	0.1178	0.11433	0.15069
		20~30	0.00670	0.00676	0.0073	0.00758	0.00676
3		0~10	0.28980	0.35746	0.54099	0.40973	0.42095
		10~20	0.00710	0.01905	0.02626	0.06789	0.06254
		20~30	0.00660	0.00743	0.00710	0.00729	0.00652
1	Soluble	0~10	0.15597	0.10870	0.18429	0.19448	0.18957
		10~20	0.00650	0.02986	0.05682	0.07688	0.07512
		20~30	0.00570	0.00750	0.00599	0.03237	0.02011
2		0~10	0.05090	0.14437	0.18230	0.16161	0.34672
		10~20	0.00640	0.01293	0.02950	0.03384	0.05542
		20~30	0.00610	0.00585	0.00630	0.00576	0.00660
3		0~10	0.09090	0.12999	0.19151	0.12313	0.15599
		10~20	0.00630	0.00859	0.00799	0.02078	0.02210
		20~30	0.00570	0.00614	0.00499	0.00614	0.00588

Table 7

Diffusion coefficient (D_c) of studied concretes ($x10^{-7}$ cm^2/sec).

Mix No.	1-month	2-month	3-month	4-month	5-month
1	1.34	0.965	0.552	0.451	0.439
2	1.23	0.617	0.544	0.420	0.336
3	1.13	0.602	0.446	0.391	0.324

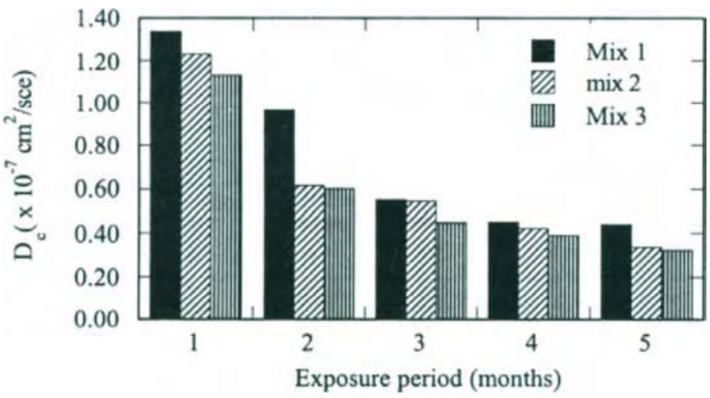


Figure 5. Diffusion coefficient of chloride ions for the studied mortar.

Table 8

Summary of pore structure data of mortar at 28 and 90 days.

Measured property	28 - days			90 - days		
	Mix 1	Mix 2	Mix 3	Mix 1	Mix 2	Mix 3
Total pore volume, cc/g	0.0929	0.0956	0.1006	0.0869	0.1017	0.1067
Total porosity, %	6.5126	6.6957	7.2698	6.1634	7.2698	7.4697
Total pore surface area, sq-m/g	13.094	15.1870	17.7980	14.6660	19.263	21.812
Average pore diameter, μm	0.0248	0.0252	0.0226	0.0237	0.0211	0.0196
Median diameter (volume), μm	0.0732	0.0435	0.0363	0.0524	0.0338	0.0260
Median diameter (area), μm	0.0103	0.0107	0.0099	0.0095	0.0093	0.0098

The diffusion coefficient results of chloride ions into the concrete studied support the fact that the diffusion coefficient is affected by replacing the OPC with RHA. From Table 7 and Figure 5, it is evident that diffusion coefficient values decrease with increasing the replacement percent of RHA and the diffusion coefficient values of RHA concretes are lower than those of OPC concrete at all the exposure periods.

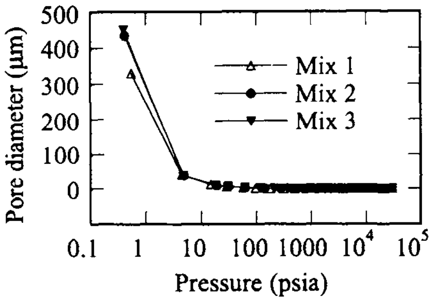
6. PORE STRUCTURE OF RHA MORTAR

The resistance of cementitious materials to chemical attack or physical degradation is related to the mechanical properties of the material, but more importantly the chemical and microstructural characteristics and particularly the pore structure of the hardened material [23]. Therefore, three mixtures of OPC and RHA mortars were made with the same mix proportions of the concrete studied without coarse aggregate (see Table 2). The properties studied include the pore structure of mortar which involved, porosity, total pore volume, total pore surface area, and pore size distributions. The most important output data of Mercury Intrusion Porosimetry (MIP) are summarized in Table 8.

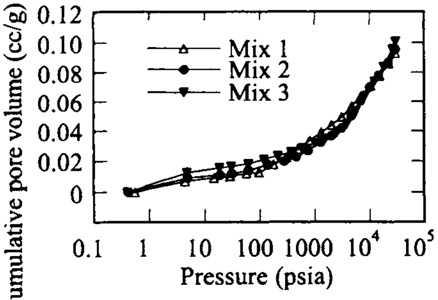
The results obtained show that the pore volume increases with the increasing RHA content and this confirms the previous notes reported by Roy [24]. Also, the pore volume of OPC mortar gives lower values than those of RHA mortar. This is due to the same reasons mentioned by Roy, where, adding RHA as mineral admixture leads to decrease in pore size or increase in the fraction of porosity in the finer pore. The RHA mortars indicate higher values of pore surface area than those of the OPC and the measured pore surface area increased with the increased RHA content due to the existance of more fine pores.

The mortar of OPC mix shows lower porosity than the range of OPC mortar reported by Raymond[25]. Further, porosity of RHA mortars shows higher values than those of the OPC mortar mix and total porosity increases with an increase in RHA content. Using RHA cement affects the properties of product mortar, therefore, the open channels are blocked by the effect of RHA and hydration products, leading to a change of pore structure such as the formation of finer and discontinuous pores. Moreover, the obtained results demonstrate the importance of curing on the properties of studied mortar.

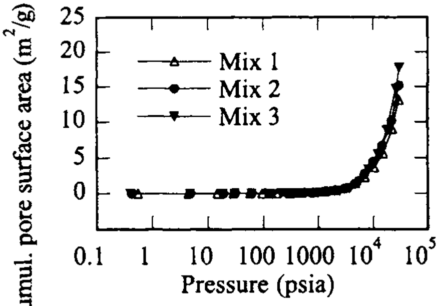
The profiles curves of the relationships between the applied pressure and measured pore diameter, cumulative pore volume, cumulative pore surface area, and cumulative porosity at 28 days and 90 days for the mortars studied are shown in Figure 6 and Figure 7, respectively.



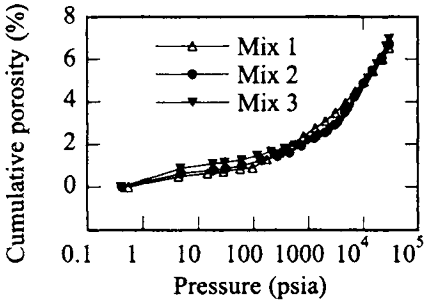
(a) Pressure vs. pore diameter



(b) Pressure vs. cumulative pore volume

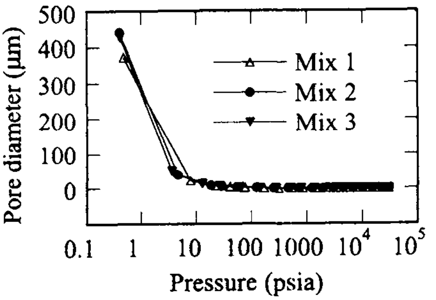


(c) Pressure vs. cumul. pore surface area

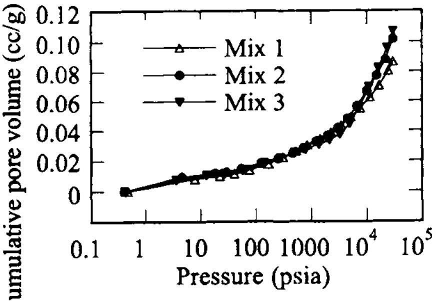


(d) Pressure vs. cumulative porosity

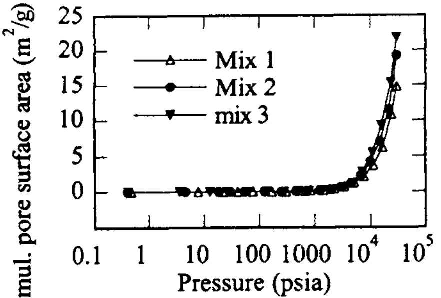
Figure 6. Profile curves at 28 days.



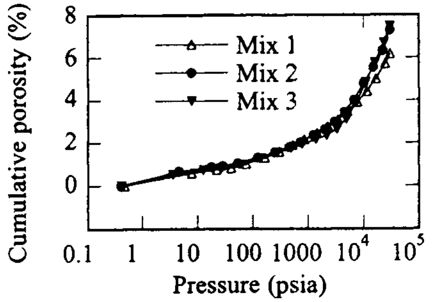
(a) Pressure vs. pore diameter



(b) Pressure vs. cumulative pore volume



(c) Pressure vs. cumul. pore surface area



(d) Pressure vs. cumulative porosity

Figure 7. Profile curves at 90 days.

7. CONCLUSIONS

1. The properties of RHA varies depending on burning and grinding methods. Moreover, The initial and final setting times of OPC-RHA pastes are affected due to adding RHA. Furthermore, the chemical composition of RHA satisfies the ASTM C618-78 requirements for chemical composition.
2. The compressive strength of concrete decreases with increasing RHA content up to 28 days. After that, RHA concretes show the same or higher strength than those of an OPC mix. Therefore, concrete containing RHA exhibit higher long term strengths and better durability.
3. RHA has its special properties and good influence in concrete properties especially those controlling the durability such as low chloride ion permeability and low diffusion in concrete. Total chloride contents indicate that RHA concrete outperform the concrete of OPC alone and its levels show large reductions as the depth of concrete zones surveyed increased. Therefore, RHA concrete may require less depth of cover to protect the reinforcing steel than those concretes using OPC alone.
4. The addition of RHA as blending materials improves the different characteristics of product concrete due to both chemical reactions and physicochemical effects. The open channels are blocked by the effect of RHA and hydration products, leading to change of pore structure such as the formation of finer and discontinuous pores.

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G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Modelling the effects of waste components on cement hydration

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Ordinary Portland Cement (OPC) is often used for the Solidification/Stabilization (S/S) of waste containing heavy metals and salts. These waste componenents will precipitate in the form of insoluble compounds onto unreacted cement clinker grains preventing further hydration. In this study the long term effects of the presence of contaminants in solidified waste is examined by numerically simulating cement hydration after precipitation of metal salts on the surface of cement grains. A cement hydration model was extended in order to describe porewater composition and the effects of coating. Calculations were made and the strength development predicted by the model was found to agree qualitatively with experimental results found in literature. The complete model is useful in predicting the strength and leaching resistance of solidified products and developing solidification recipes based on cement.

1. INTRODUCTION

Ordinary Portland Cement (OPC) is often used for the Solidification/Stabilization (S/S) of waste. Waste components can retard or even stop the hydration of cement by precipitation of insoluble compounds on the partly hydrated cement particles [1]. Yousuf et al. [2] describe a "Charge Dispersal Model" in which zinc hydroxide anions are dispersed by the presence of OH^- ions in the cement porewater. Because the negative cement surface is charge-compensated by Ca^{2+} ions, a diffuse layer of negative zinc hydroxide anions is present and will be transformed into calcium zincate which completely coats the cement particles with an impermeable layer and thus inhibits further hydration reactions. Experiments with cadmium and lead showed that coating took place in the first minutes after mixing cement, water and waste [3].

This coating mechanism can be modelled using a cement hydration computer model that was developed at NIST [4]. In this model a hydrating cement paste is represented by a digital matrix of pixels with a unit size of 1 μm^3 , which are assigned to water, gypsum or one of the cement mineral phases or possible reaction products. A simulation consist of dissolution cycles in which solid phases are scanned and can dissolve, react, diffuse and precipitate as CH or calcium-silicate hydrate (CSH). After a large number of hydration cycles it predicts the hydration degree, the porosity and the phase composition of the solid structure. In order to simulate cement hydration in the presence of waste components, it is important to consider the porewater composition. The chemical equilibria of interest are strongly dependent on the presence of common ions in cement porewater such as Ca^{2+}, K^+, Na^+ and OH^-. Based on these equilibria, the pH and the amount of precipitate can be determined.

2. POREWATER CONCENTRATIONS

The pore solution is assumed to be saturated in $Ca(OH)_2$ during cement hydration. During cement hydration high amounts of alkalis, sodium and potassium, are released. While the ion products of both KOH and NaOH are significantly higher compared to that of $Ca(OH)_2$, it is assumed that the solution is always saturated with regard to the latter. Thus, given the total concentration of alkali released (sum of Na^+ and K^+) into the porewater and the known ion product for $Ca(OH)_2$ it is possible to calculate $[OH^-]$ and $[Ca^{2+}]$ concentrations as a function of hydration degree.

Taylor [5] developed a method to describe the alkali content in cement pore water. It is based on the total alkali content in cement, the w/c ratio used and the hydration degree. When the release and uptake of alkalis and the porosity fraction is known, the concentration of alkalis and corresponding OH^- can be predicted during hydration.

For most Portland cements the Na_2O equivalent is given, which is the mass percentage of Na_2O that would produces the same amount of moles of alkali as the sum of Na_2O and K_2O mass present in cement. All calculations will be based on this equivalent as if the amount of alkali released only consists of Na^+.

The total number of moles of alkalis per gram cement is:

$$Na_T = \frac{Na_{eq} \cdot 2}{M_{Na_2O}} \tag{1}$$

Na_T = alkali content in [mole/g]
Na_{eq} = Na_2O equivalent [g/g]
M_{Na_2O} = molecular mass Na_2O = 62 [g/mole]

Assuming that alkalis are released linearly proportional with hydration degree, the total alkali concentration released in the pore solution, is calculated as follows:

$$[Na^+]_{released} = \frac{Na_T \cdot \alpha \cdot m_c}{\frac{\phi_{por}}{\phi_{por}^0} \cdot \frac{m_w}{\rho_w}} = \frac{Na_T \cdot \alpha}{\frac{\phi_{por}}{\phi_{por}^0} \cdot w/c} \cdot \rho_w \tag{2}$$

$[Na^+]$ = alkali released in [mole/l]
α = hydration degree
m_c = mass cement in [g]
m_w = mass water in [g]

$\frac{\phi_{por}}{\phi_{por}^{0}}$ = concentration factor

ρ_w = water density = 1000 [g/dm^3]

w/c = water/cement ratio

The concentration factor, defined as the ratio of the porosity fraction to the initial porosity fraction is used to account for the decrease in porosity during hydration and is therefore α dependent. As a result of this decrease in porosity all ions present in the pore solution are concentrated correspondingly. In Taylor [5] it is discussed that the amount of each alkali cation taken up by the hydration products CSH and AFm phase is proportional to the concentration present in the solution and the quantity of these hydration products formed. All alkalis are both released and consumed with equivalent amounts of OH^- ions. Taylor introduced two empirical constants, called binding factors, which are numerically equal to the amount of alkali in mmole that can be taken up from a 1 M alkali solution by the total quantity of hydration products formed from 100 g OPC. Although the consumption rates for Na^+ and K^+ will not be exactly the same an estimated mean value of 0.23 mmole alkali per g OPC per mole alkali per liter porewater will be used here. Hence the amount of alkalis consumed in mole/l is:

$$[Na^+]_{consumed} = \frac{b_{Na} \cdot \alpha \cdot m_c \cdot [Na^+]_{released}}{m_w} = \frac{b_{Na} \cdot \alpha}{w/c} \cdot [Na^+]_{released} = \frac{b_{Na} \cdot Na_T \cdot \rho_w \cdot \alpha^2}{\frac{\varphi_{por}}{\varphi_{por}^{0}} \cdot (w/c)^2} \quad (3)$$

b_{Na} = alkali binding factor = 0.23 [ml/g]

The difference between the amounts of alkali released and consumed gives actual alkali pore concentration.

$$[Na^+]=[Na^+]_{released}-[Na^+]_{consumed} \quad (4)$$

The pore solution is saturated with respect to CH. The corresponding activity product was taken from SOLTEQ [6], the chemical equilibrium model developed by Batchelor and Wu, based on MINTEQA2 [7]. The corresponding activity coefficients were calculated using the Davies Equation for single ions [8]. The corresponding solubility product is then:

$$k_l = [Ca^{2+}][OH^-]^2 = 2.70 \cdot 10^{-5} \quad (5)$$

If excess of a solid phase is in equilibrium with the solution, the total amount of that compound in solution is called the molar solubility, denoted by S [8]. In a solution that contains $Ca(OH)_2$, the molar solubility is denoted S_{CH}.

In a saturated solution of an ionic salt, addition of another, more soluble salt containing one of those ions, will decrease the solubility of the first. This is known as the "common-ion effect". The $[OH^-]$ ions in solution originates both from the dissolution of $Ca(OH)_2$ and from the amount of alkali released into the porewater. As long as solid CH is present the following relations should hold:

$$[Ca^{2+}] = S_{CH} \tag{6}$$

$$[OH^-]=2 \cdot S_{CH} + [Na^+] \tag{7}$$

Substituting Eqs. (6) and (7) into the solubility product k_1 (Eq. (5)) gives the following equation:

$$k_{CH}=[Ca^{2+}]\cdot(2[Ca^{2+}]+[Na^+])^2=4[Ca^{2+}]^3 + 4[Na^+][Ca^{2+}]^2 +[Na^+]^2[Ca^{2+}] \tag{8}$$

For a known alkali concentration this equation is dependent in $[Ca^{2+}]$ only and was solved analytically using the computer program MATHEMATICA® [9]:

$$[Ca^{2+}] = \frac{([Na^+]-X)^2}{6 \cdot X} \tag{9}$$

$$X = \sqrt[3]{([Na^+]^3 + 27 \cdot k_{CH} + 3\sqrt{3} \cdot \sqrt{k_{CH}} \cdot \sqrt{2 \cdot [Na^+]^3 + 27 \cdot k_{CH}})}$$

When $[Ca^{2+}]$ is calculated, $[OH^-]$ can be calculated from the solubility product and the pH can be determined from the relation pH = 14 + log$[OH^-]$.

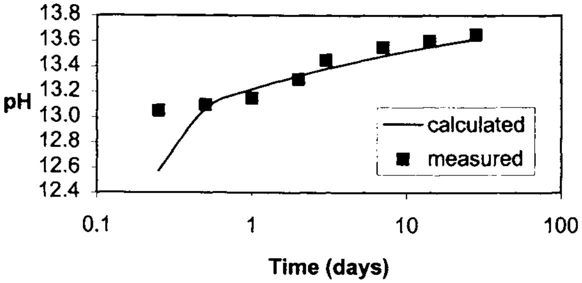

Figure 1. Porewater pH development

Figure 1 shows the calculated pH development compared with experiments by Pietersen [10]. As can be seen from this figure there is a good agreement from 1 to 28 days of hydration. The disagreement during the first hours of hydration can be explained by the observed supersaturation of CH [5]. This was not accounted for in the calculations.

3. THE PRINCIPLE OF COATING LAYERS

It is assumed that as soon as cement and water containing the contaminant are mixed, precipitation will occur. According to the chemical equilibria an amount of precipitated product will be formed and this amount or volume will coat the unhydrated cement surface. This results in part of the cement surface being inaccessible for water. Furthermore it is assumed that the precipitated volume is made up of layers of cubic units sized $d_{layer} \cdot 1\ \mu m \cdot 1\ \mu m$. The average number of coating layers present on the initial surface of the cement particles is dependent on the initial amount of precipitated product and can be calculated according to equation (10):

$$n_{layers} = \frac{\varphi^{p}_{pp}}{d_{layer} \cdot SA \cdot \rho_{pp}} \qquad (10)$$

n_{layers} = average number of coating layers
φ^{p}_{pp} = mass fraction precipitated product precipitated [g/g of cement]
d_{layer} = coating layer thickness [cm]
SA = specific surface area of cement [cm^2/g]
ρ_{pp} = precipitated product density

During cement hydration the following mass balance should be obeyed, in which all fractions are in [g/g] unreacted cement:

$$\varphi^{T}_{pp} = \varphi^{s}_{pp} + \varphi^{p}_{pp} \qquad (11)$$

φ^{T}_{B} = total initial mass fraction precipitated product [g/g OPC]
φ^{s}_{B} = mass fraction precipitated product (re)dissolved [g/g OPC]

φ^{T}_{B} can be calculated from Eq.(11), filling in the theoretical total amount of precipitate in [$mole/dm^3$] that can be formed from the product added, taking into account possible molar differences, and concentration factor = 1. φ^{s}_{B} is calculated from the equilibrium concentration of precipitate that is determined after each hydration cycle.

$$\varphi^{p}_{pp} = \frac{m^{p}_{pp}}{m_c} = \frac{[pp] \cdot w/c \cdot \frac{\varphi_{por}}{\varphi^{0}_{por}} \cdot M_{pp}}{\rho_w} \qquad (12)$$

m_B^P = mass precipitated product [g]
m_c = mass cement [g]
[pp] = amount of precipitated product [$mole/dm^3$]

$\frac{\phi_{por}}{\phi^0_{por}}$ = concentration factor (ratio actual porosity to initial porosity)
M_{pp}=molecular mass precipitated product [g/mole]
ρ_w = density water [g/dm^3]

When the total volume of precipitate is known, it has to be placed at the water exposed surface of the unhydrated cement particles. In the hydration model, the smallest size unit is 1 μm^3 and the water exposed surface consists of m_s surface planes of 1 μm^2. Then the total volume of precipitate consists of n units of volume d_{layer} times 1 μm^2 that have to be placed randomly on the cement particle surface. Subsequently, from statistics [11] one can compute the surface fraction p(x) that is coated by x units after placing the total of n units. The probability p that one unit is placed on one specific surface plane is inversely proportional to the number of surface planes m_s, so $p = 1/m_s$. The surface fraction that remains uncoated, denoted as p(0) can be calculated as follows:

$$p(0) = (1-1/m_s)^n \qquad (13)$$

Note that taking a surface of $m_s = 100$ and taking the corresponding total number of units n as $100 \cdot n_{layers}$ is sufficient to produce accurate results for the probabilities of interest. From equation (13) it follows that when the cement surface could be coated by more than 5 coating layers on average, and using the probabilistic placement procedure proposed here, the percentage of uncoated surface decreases to less than 1%. From preliminary simulations it followed that reasonable hydration rates take place when 5% of the surface is uncoated, corresponding with a probabilistic distribution of 3 coating layers in average.

4. COMPUTATIONAL RESULTS

As an example the well-known retarding effects of borates will be described according to the model developed in this work. Calcium diborate $Ca[B(OH)_4]_2.2H_2O$ (CBH6 in cement chemistry notation) is formed instantaneously after mixing cement and borate containing water, as a result of the high pH and high calcium concentration in the porewater. When boric acid (H_3BO_3) is dissolved in the porewater, it forms $[B(OH)_4^-]$ ions and in the presence of Ca^{2+}, the equilibrium of interest is the following [12]:

$$Ca[B(OH)_4]_2\,(s) \Leftrightarrow Ca^{2+} + 2\,[B(OH)_4^-] \qquad (14)$$

$$k_2=[Ca^{2+}][B(OH)_4^-]^2 = 1.62 \cdot 10^{-6}\ [mol^3/dm^3] \qquad (15)$$

Defining S_{CH} and S_{CBH6} as the molar solubilities of CH and CBH6 respectively, yields the following concentration balances:

$$[B(OH)_4^-] = 2 \cdot S_{CBH6} \qquad (16)$$

$$[Ca^{2+}] = S_{CH} + S_{CBH6} \tag{17}$$

From rearranging both equilibria (5) and (15) and all relevant concentration balances and substituting the results back in equation (5), yields the following equation in which $[B(OH)_4^-]$ is the only variable in case $[Na^+]$ is known:

$$k_2 = (S_{CH} + S_{CBH6}) \cdot [B(OH)_4^-]^2 = K \cdot [B(OH)_4^-]^3 - \frac{1}{2} \cdot [Na^+] \cdot [B(OH)_4^-]^2 \tag{18}$$

$$K = \frac{1}{2} \cdot \sqrt{\frac{k_1}{k_2}} + \frac{1}{2}$$

In case of a known alkali concentration the solution of this cubic equation in $[B(OH)_4^-]$ in closed-form is as follows (based on analysis by MATHEMATICA® [9]):

$$[B(OH)_4^-] = \frac{[Na^+] + X}{6 \cdot K} + \frac{[Na^+]^2}{6 \cdot K \cdot X} \tag{19}$$

$$X = \sqrt[3]{([Na^+]^3 + 108 \cdot k_2 \cdot K^2 + 6\sqrt{6} \cdot \sqrt{k_2} \cdot K \cdot \sqrt{[Na+]^3 + 54 \cdot k_2 \cdot K^2})}$$

When $[B(OH)_4^-]$ is determined, $[Ca^{2+}]$ can be calculated according to the ion product k_2 and $[OH^-]$ can be calculated using the ion product k_1.

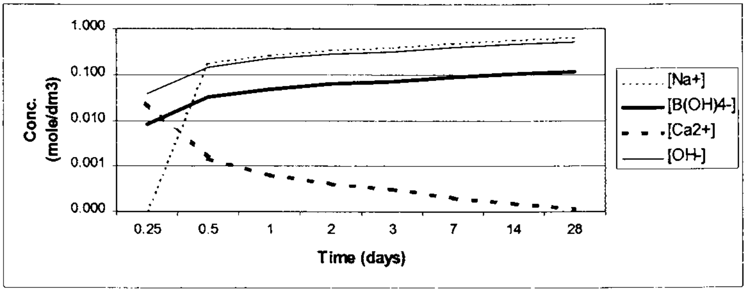

Figure 2. $[Na^+]$, $[B(OH)_4^-]$, $[Ca^{2+}]$ and $[OH^-]$ plotted against time.

In Figure 2, the development of porewater concentrations during undisturbed hydration is plotted against time. When hydration starts, $[Ca^{2+}]$ is high and $[B(OH)_4^-]$ must be low because of its ion product and CBH6 precipitates. Then alkalis are released by cement and $[Na^+]$ and correspondingly $[OH^-]$ in the porewater increase. This results in a decrease in $[Ca^{2+}]$ because of the CH ion product. As a result of this CBH6 can redissolve, the surface coating percentage decreases, hydration rate will increase and more alkali are released. This is a self-accelerating process. From these equilibria it is also clear that when coating percentages approach 100%, the hydration rate is too slow to release sufficient alkalis for redissolution of the coating compound. In that case hydration is completely stopped.

From experiments by Lieber and Richartz [13] it is known that hydration can finally proceed, even when pollutant additions up to 1 mass% are used. Assuming that the crystal layer thickness $d_{crystal}$ is equal to the unit cell size of the CBH6 crystal (about $6 \cdot 10^{-10}$ m), this addition would correspond with 39 coating layers. According to equation (21), this corresponds with a completely coated surface and hydration would be stopped completely. From this observation it is assumed that the minimum precipitation layer thickness d_{layer} is build up from a number of crystal layers ($n_{crystal}$) with the size of one crystal unit of CBH6 ($n_{crystal}$), so $d_{layer} = n_{crystal} \cdot d_{crystal}$.

The equilibria and coating mechanism described above were implemented in the cement hydration model. When concentrations are calculated during cement hydration it is assumed there is an equilibrium at the end of every hydration cycle. All parameters were chosen according to the experimental conditions used by Lieber and Richartz [13], who examined the effect of boric acid on setting properties and strength development of Portland cement. They used OPC with a SA of 4080 [cm^2/g], a Na_{eq} of 0.92%, a w/c ratio of 0.5 and borate concentrations of up to 1 mass% (g H_3BO_3 per g OPC). $n_{crystal}$ was estimated as 13, so that the 1% addition corresponded with 3 coating layers in average.
Before cement hydration starts, the total initial $[B(OH)_4^-]$ and φ_B^p at $[Na^+] = 0$ is calculated. A digital initial cement microstructure is generated and the cement particle surface is coated according to the probabilistic placement procedure. After performing this procedure, only the uncoated surface planes are initially available for dissolution and reaction.
After each hydration cycle, the α and actual porosity of the cement paste is given by the cement hydration computer model and all parameters of interest can be calculated in the order, $[Na^+]$, $[B(OH)_4^-]$, φ_B^s and φ_B^p. According to this recalculated φ_B^p , a corresponding removement of coating from the cement surface is performed. This is done by randomly decreasing the number of coating units from surface planes that are coated by 1 or more coating units. This adjustment results in an increase in uncoated surface planes, making them available for dissolution in the following hydration cycles. H_3BO_3 additions of 1.0, 0.5, 0.2 and 0.1% were used in the simulations and hydration was allowed to proceed to an equivalent hydration time of 28 days.

In Figure 3 the hydration degree is plotted against time and one can see a clear difference between the lower 0.1 and 0.2% and the two higher 0.5 and 1.0% pollutant additions. For the higher 1 and 0.5% additions, initially hydration degrees are significantly lower compared to the blank sample. After two or three days their hydration rates increase, while hydration rate of the blank sample is decreasing. At 28 days there was still precipitate and thus coated surface present in both cases. It can be expected that, while hydration continues, all remaining precipitate will redissolve and final hydration degrees degree will be comparable to the blank sample. For the two lower additions 0.2 and 0.1%, the initial coating percentages were less than 50%, which results in a much quicker initial hydration rate and redissolution of precipitate compared to the other polluted samples. This results in hydration rates that are comparable to the blank sample. The trends found in the simulations agree qualitatively with the experimental results by Lieber and Richartz [13], who measured strength development. Strength was calculated from the hydration degree given by the model using the gel-to-porosity principle, calculated as follows [14]:

$$X = \frac{0.68 \cdot \alpha}{0.32 \cdot \alpha + w/c} \tag{20}$$

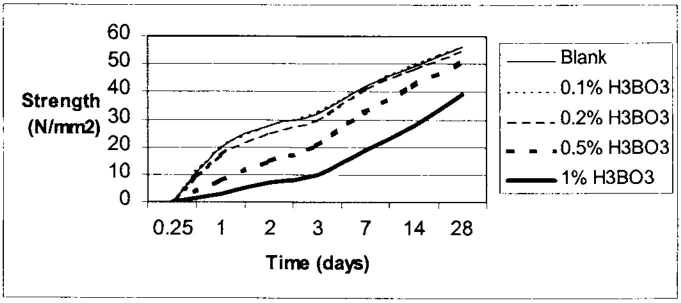

Figure 2: Computed strengths at different pollutant concentrations versus time

For the higher H_3BO_3 concentrations added, strength was decreased at ages less than 3 days, but approached blank values after 28 days. The 0.1 and 0.2% additions showed equal strength development compared to the blank sample. These result agree qualitatively with experimental results from Lieber and Richartz [13].

5. CONCLUSIONS

Based on chemical equilibria of calcium salts in the presence of alkalis, quantities of precipitates were computed. It is shown that depending on the hydration degree and related alkali release, calcium salts will precipitate and redissolve. This precipitation model has been incorporated in a numerical cement hydration model and results were compared with experimental data of calcium borates. This yielded good qualitative agreement. An important unknown is the number of crystal layers per coating layer. We have assumed this value to be equal to 13, but this should be validated experimentally. This number is an important parameter that is required for relating used pollutant concentrations and layer thicknesses initially present on the cement surface. The approach presented here can also be used to describe the retarding effects of common pollutants like Cd and Zn. More research and calculations are required so that in the future hydration in the presence of pollutants can be predicted, taking into account experimental parameters like w/c ratio and specific cement surface area, pollutant concentrations in the mixing water and chemical equilibria of all ions involved. In that case immobilization recipes can be optimized and durability of the solidified product can be predicted.

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Leaching behaviour of synthetic aggregates

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In the framework of EU project Utilising innovative kiln technology to recycle waste into synthetic aggregate (BRST-CT98-5234), the leaching behaviour of synthetic aggregates has been studied to assess its environmental compatibility in the various stages of its use. Since the conditions are very different for the different uses, the assessment calls for a variety of different leaching conditions. The pH dependence test is used to cover important differences in pH environment to which the materials are exposed to as well as for an assessment of the buffering capacity of the material. Synthetic aggregate features a low buffer capacity, which makes it sensitive to externally imposed pH conditions. Utilisation and storage exposed to acidic conditions needs to be avoided. The pH dependence test and column leaching test are consistent. The CEN TC 154 method appears provide systematically low values due to the arbitrary selection of test conditions. Synthetic aggregate studied to date will not adversely affect the concrete in its service life. The main issue for aggregate use is the recycling and the "end of life" condition, when the material becomes construction debris. Not metals, but oxyanions, such as Cr VI and Mo are most relevant under these conditions. A concise test has been applied to assess crucial aspects of leaching for different production mixes.

1. INTRODUCTION

In the framework of EU project Utilising innovative kiln technology to recycle waste into synthetic aggregate (BRST-CT98-5234), a new kiln design with a more efficient energy use is applied, which has more flexibility to process different waste materials as feedstock. The starting materials and the synthetic aggregates produced at laboratory scale at the School of Civil Engineering (Leeds) and at full scale facility in the south of England were tested for their leaching behaviour to assess their environmental compatibility in the various stages of their use. This includes storage prior to use, use as an aggregate in concrete, its recycling as construction debris in the same application, its reuse in other applications (e.g. road base construction) and its end-of-life situation (ultimate disposal). In all of these phases of use, the release of constituents from the material needs to be addressed to ensure environmental compatibility. Since the conditions are very different for the different uses, the assessment calls for a variety of different leaching conditions. Monolith leaching tests for bound applications [1,2] and percolation test [3,4] for several others. The pH dependence test [5] is used to cover important differences in pH environment to which the materials are exposed to as well as for an assessment of the buffering capacity of the material, which provides insight in the sensitivity of the materials to externally imposed conditions. In the framework of CEN TC 154, a compliance test for aggregates has been drafted, which contains an arbitrary choice of conditions unrelated to potential environmental impact. This method has been tested as well to verify its performance relative to the more elaborate evaluation.

2. EXPERIMENTAL WORK

2.1 Materials

A range of materials have potential for use as feedstock for the aggregate production: granite washings, paper sludge, contaminated river sediment, MSWI bottom ash and shredder waste. The suitability of these materials in preparing pellets meeting technical specifications is studied at the School of Civil Engineering (Leeds). A key aspect is the water uptake of the pellets. The starting materials - sediments, municipal solid waste incinerator bottom ash (MSWI BA), shredder waste, milling residues, paper sludge - have been tested using the pH dependence test to identify the main leaching features of the starting materials for later comparison with the behaviour of pellets produced. Synthetic aggregate pellets, produced by firing in an innovative kiln at lab-scale from several combinations of sediment, municipal solid waste incinerator bottom ash, shredder waste, milling residues and paper sludge, and aggregates resulting from full scale aggregate production have been tested using the pH dependence test and the concise leaching test. On limited number of samples (due to large material amount required) the TC 154 method has been applied. On an aggregate sample from granite washings all tests including a column test on the intact pellets has been carried out. From a limited number of aggregate samples concrete specimen have been prepared and tested using the tank leaching test [1], a compliance tank leaching test [2] and the pH dependence test [5]. This allows an evaluation of the material in different stages of use, such as storage prior to use, use as an aggregate in concrete, its recycling as construction debris in the same application, its reuse in other applications (e.g. road base construction) and its end-of–life situation (ultimate disposal).

2.2 Methods

The leaching tests selected for the study are:

- pH static leach test [5]: This test provides information on the pH sensitivity of leaching behaviour of the material. The test consists of a number of parallel extractions of a material at a liquid/solid ratio (L/S) 10 (l/kg) during 48 hours at a series of preset pH values. Since pH is one of the main leaching controlling parameters, the information can be used to evaluate the repeatability in testing (resulting from measurement at steep concentration - pH slopes) and to provide information on the sensitivity to pH in specific field scenarios. The acid neutralization capacity (ANC) derived from the test is a useful property in this respect. For material characterization this has been proven to be a very useful method [6,7]. The method is standardized in two experimental modes by CEN TC 292 Working Group 6.
- Column leaching test with similarities to NEN 7343 [3] and a percolation test is developed at European level in CEN TC 292 WG6 [4], a column test in which 7 eluate fractions are collected within the range of L/S = 0.1-10 l/kg. The total test duration is approximately 21 days. The leachant is demineralized water (DMW). The test material is applied as received (around 1 cm ∅) and upflow (14 ml/hr) is applied through a column waste height of 28 cm and a diameter of 10 cm.
- NEN 7345 Tank leach test [1]: In this test the specimen is subjected to leaching in a closed

tank. The leachant is renewed after 8 hours, 1, 2.25, 4, 9, 16, 36, 64 days at a leachant to product volume ratio (L/V) of approximately 5. The results are expressed in mg/m2. This test is a procedure to evaluate the release from monolithic material by predominantly diffusion control (e.g. exposure of structures to external influences). The distinction is necessary as the transport limitations set by a solid form result in a significantly lower environmental impact than derived from crushed material. This condition is valid as long as the product retains its integrity. To assess the behaviour after disintegration or demolition of monolithic forms, the information obtained in the pH static leach test is very relevant, as in this situation the pH is likely to change to more neutral conditions.

- Compliance monolith leach test [2]. Although still in development by CEN TC 292 WG2 the main test features are: the specimen is leached after vacuum saturation with demineralised water at an liquid to area ratio of 5, eluates are produced after 6, 24 and 48 hours and subsequently analysed.
- Compliance test for aggregates as developed in CEN TC 154 Aggregates[8]. This method consists of a leaching of the aggregate at a liquid to solid ratio of 10 (l/kg) for 24 hours. For this purpose the aggregate is placed on a grid above a magnetic stirrer. No particle size requirements are provided to limit the contribution of fines.
- Concise leaching test [9], which has been proposed to address the main factors relevant to leaching from waste. It consists of four extractions for 24 hours at L/S=1 and L/S=10 at the material's own pH and two subsequent extractions at L/S=10 under pH control at pH=4 and neutral pH (or mild alkaline pH, when the material is neutral by itself).

2.3 Data treatment

The pH dependence test data are used as a basis of reference for data from other tests [6]. The data on the column percolation test are given as a function of the L/S. The relevant data from the compliance tests are inserted in these respective graphs. In the graphs, the regulatory criteria for granular materials (Category I and Category II of the Building Materials Decree [10]) are inserted for evaluation of critical nature of constituents. The data from the pH dependence test are used for geochemical modelling of potential solubility controlling minerals (not addressed here). The release from the intact pellets is addressed taking into account the diffusion from the interior of the pellets. For this purpose measurements were extended in one series up to several days of leaching. The release from concrete specimen is addressed to assess the contribution of aggregates to the overall material properties during both service life, recycling and "end of life" conditions.

3. RESULTS

3.1 Original wastes

Granite washings – Granite washings are not critical from a leaching point of view for any of the parameters measured (about 28) according the Dutch Building materials Decree [10].

Paper sludge - Paper sludge is characterized by a very high TOC (dissolved organic carbon) and a relatively high TIC (carbonate). The elements Se, Mo, Ba and Cu only at pH > 10 exceed critical regulatory limits [10]. The material has a strong buffering capacity, as the amount of acid needed to increase the pH one pH unit is quite significant (2 Mol/kg).

Shredder waste - The buffer capacity of shredder waste is relatively small. This implies that the material is sensitive to both acid and base influences. For instance in case of Zn, a small change in acid addition will lead to a significant increase in Zn leachability (more than

1 order of magnitude for 0.1 Mol/kg). The elements Cu, Cd, Mo, Sb, Zn and Pb exceed the regulatory criteria [10] over a large portion of the pH range studied. Cr and Sn become critical at high pH, whereas Ni and Co become critical at low pH. TOC shows a characteristic increase for many materials containing organic matter (increase of TOC with increasing pH).

Harbour sediment - A small change in acid addition leads to a quite significant change in Zn leachability. The acid amount required to reach a pH below 5 is substantial. The agreement between CEN test data and the pH stat data are generally good. A duplicate analysis also leads to repeatable results, unless the concentrations become low and analytical detection starts to play a role. For various elements it is clear that a relatively small change in pH may lead to very significant changes in leachability. Ni, Co and Zn show several orders of magnitude change within one to 2 pH units.

MSW Incinerator bottom ash – Much information is available on this material [6,11,12], which indicates that Cu, Mo, Cl and Sb are potentially critical.

In comparison with leaching data on synthetic aggregates produced from mixtures of wastes, generally significantly lower leachability is observed for many constituents.

3.2 Characterization of synthetic aggregate produced from waste

The synthetic aggregates produced from one or a combination of the various waste streams have been tested for their leaching behaviour with several leaching tests, of which the pH dependence test proves to be the most versatile one. This test provides besides information on the pH dependence information on the acid neutralization capacity. In figure 1 the acid/base neutralization capacity for two typical aggregates is given. The sensitivity of this material to external pH influences is considerable as the acid neutralization capacity is quite low. When the aggregate is used in concrete for gravel replacement, this property has no further consequences. In storage exposed to rain, however, undesired leaching might occur.

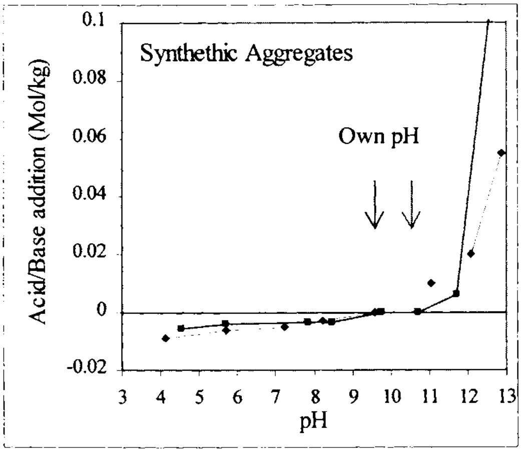

Figure 1. Acid/base neutralization for synthetic aggregates illustrating the low buffer capacity.

Two aggregate samples (a mixture of different wastes and a mixture of granite washings and paper sludge) have been subjected to a variety of different characterization leaching tests. This is done to set a reference for the behaviour of synthetic aggregate against which future properties of materials to be produced with different secondary materials can be compared. The relation between the different tests needs to established beforehand to avoid surprises later. Based on the aggregate leaching results a first identification of critical components has been made relative to criteria from regulatory practice in the Netherlands (Building Materials Decree [10]). This regulation has both criteria for granular materials as well as for intact monolithic products against which the results obtained can be judged.

The pH dependence test after size reduction (< 2 mm) of the two types of synthetic aggregates are compared to give a first indication of variability due to variation in source materials. In general, the leaching behaviour of both aggregates is quite comparable with some minor deviations (figure 2). The leaching curves as a function of pH are very consistent, which can be regarded as a characteristic for aggregate, which in its production process goes through a specific temperature – time profile.

In figure 2 the leaching as function of pH is compared with the results of a column experiment on intact aggregate pellets (upflow) and a column experiment in downflow to simulate intermittent wetting/drying cycles. In general, the cumulative leached amounts as observed in the column leach tests follow a pattern, that corresponds to solubility (slope 1 in release /LS plot) for Ba and Zn. For Mo, the potential available fraction is depleted in L/S=2. Apparently, Mo is readily solubilized in the aggregate pores and subsequently washed out. The diffusion from the interior of the particles is apparently not a limitation (sufficiently porous and thus rapid exchange, see also discussion in section 3.3).

The results for other samples of aggregate tested with a concise testing protocol[9], which are also indicated in figure 2, suggest that there is a consistent behaviour between aggregates produced from different starting materials. The aggregate production process tends to impose common characteristics in the leaching behaviour of aggregates with only individual deviations depending on the level of certain elements in the starting materials. The pH static leaching test data and the column leaching test results are internally consistent, as the cumulative leached amount at the L/S=10 in the column corresponds generally well with the pH dependence test (L/S=10) data at the corresponding pH. This feature allows translation of leaching test data from percolation tests to other exposure conditions at other pH conditions.

The data also provide for a comparison between synthetic aggregate and the starting materials. Several elements - Li, Ca, K, Mn, Ca, Sr and Ba are incorporated in the silicate matrix in the sintering process. S is lost from the material by volatilization, thus leading to a lower leachability. Most other show little difference or are somewhat increased, such as Cr, V and Co. The acid/base neutralization capacity between starting material and aggregates produced is markedly different. Due to the sintering process the neutral pellets have a very low buffer capacity. The degradation of calcite and the incorporation of Ca in the silicate structure are reasons for this change.

The concise test offers a good option for an optimized quick testing protocol for quality control of the aggregate production process. This procedure leads to results within a few days. Several crucial aspects of leaching are addressed : solubility control, wash out, pH sensitivity over a wide pH range. Some specific properties can be tested on-site (so-called on site verification tests). These may include a simple test for water uptake by vacuum saturation and a measurement of conductivity.

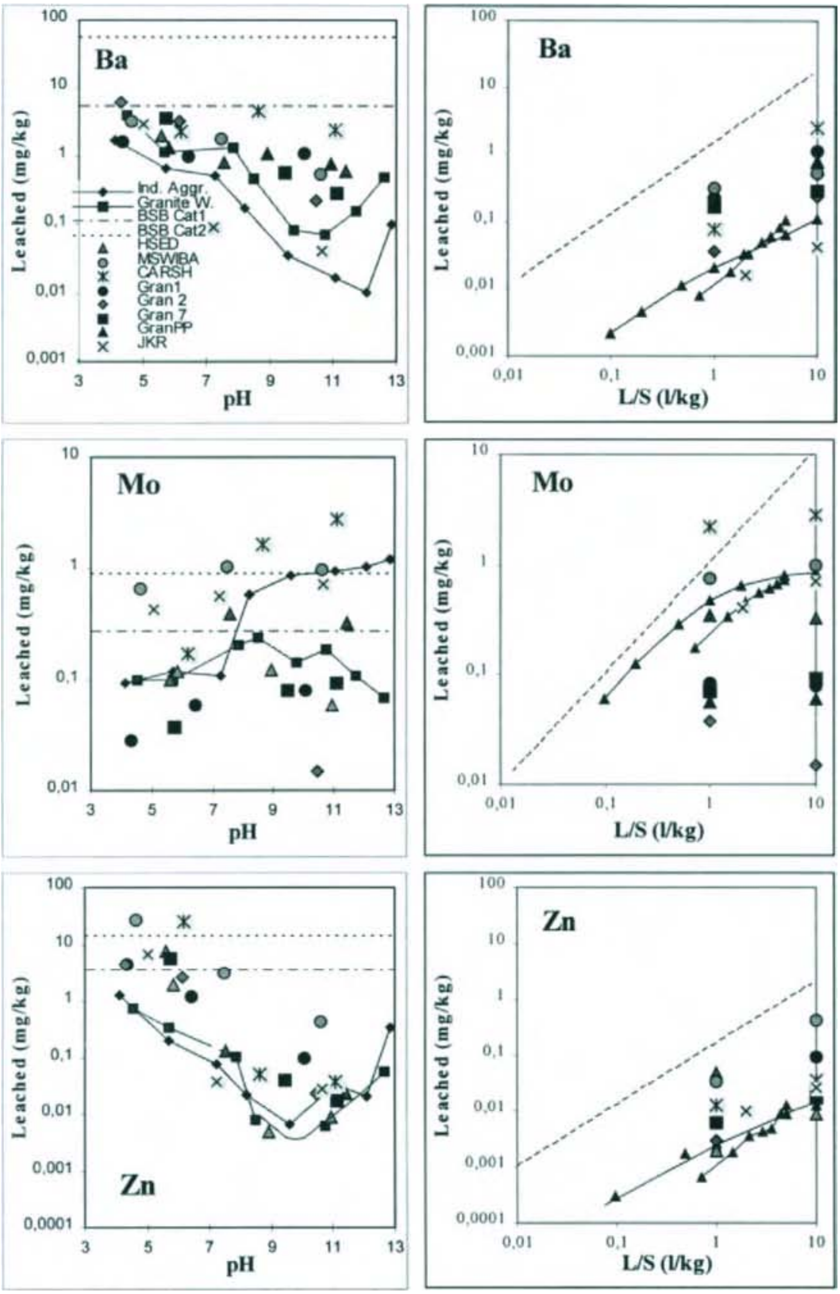

Figure 2. Leaching of Ba, Mo and Zn from aggregate as a function of pH (left) and as a function of L/S (right). Two types of triangles point at column data for intact (10mm) and size reduced aggregate pellets (< 4 mm). Slope=1 points at solubility control.

In comparison with regulatory criteria, the metals (such as Zn shown here) and Ba are of less concern than oxyanions, such as Mo (shown here), Sb and Se. For this evaluation, the relevant pH domain in application is from neutral to alkaline. The latter pH is relevant for the incorporation in concrete. When the aggregate is applied in unbound form, its sensitivity to external pH influences needs to be taken into account, which may put certain restrictions on its use in acidic environments. The increased leaching of oxyanions from sintered products is consistent with earlier observations on related materials –Lytag [13] and sintered bricks[14].

3.3 Role of diffusion from aggregate pellets in a leaching test

A key issue in the discussion on the leaching of pellets in a leaching test focuses on the particle size and the diffusion of constituents from the interior of the particles into the surrounding solution. The internal porosity is the crucial parameter here. The results from an up-flow column experiment (diameter 10 cm, height 28 cm, flow rate 14 ml/hr) on uniform aggregate (diameter around 10 mm, aggregate porosity 15 %) is compared with pH dependence test on the size-reduced aggregate (broken to < 2 mm, 24 hrs, L/S=10, own pH). In table I the results are given for the elements Al, B, Ca, K, Li, Mg, Mo, P, S, Si and Sr, which are accepted on the basis of sufficient analytical sensitivity. In the case of Ba (sufficient sensitivity), the pH difference between column and pH dependence test is important (steep gradient). Interpolation would lead to a better agreement for Ba.

After log transformation (table II) the elements that are accepted before transformation also pass, but in addition elements at relatively low concentrations, such as Co, Cr, Cu, Fe, Mn, Se and Zn show a good agreement. The rational behind the log transformation is that at low concentrations a larger tolerance is acceptable. A factor 2 difference in concentration at a level of 0.01 mg/kg is the same!! This can only be shown after log transformation. The elements Cd, Pb, Ni and Sb are too close to the detection limit to be able to draw conclusions and therefor can not contribute positively to a conclusion, but do not challenge it either. At the percolation rates applied diffusion from the interior of uniform particles up to 10 mm is fast enough in the way the column is operated (particularly the flow rate of 15 ml/hr) to provide the same end results as a batch test with size-reduced material at LS=10. Only, when the porosity of the material is low (e.g molten slag) a more significant effect of delayed release can be expected and flow rate becomes a factor. However, under that condition the question arises, if extending the running time of a column test is useful or another way of determining the contribution of diffusive release should be addressed (compacted granular leach test [15]).

In a comparison of the release at LS=10 for the column test (10 mm pellets) with the release from the same material broken to less than 2 mm at the corresponding pH (LS=10) in the pH dependence test, no significant difference is noted for several elements. By applying a log transformation, it is clear that the agreement even extends to the elements leached in low concentrations. The effect of crushing the aggregate has little effect on the leaching of elements at higher liquid to solid ratios (L/S > 2 l/kg) suggesting that the porous nature of the aggregate only leads to a relatively small delay in release. To address long term environmental impact size reduction is the better alternative for testing than running the test longer to reach a stable end point. This will also improve the repeatability of the test results.

Table I. Comparison of leaching from intact particles and equilibrium test data.

Parameter	Column (mg/kg) Intact Aggregate (d=10mm, uniform size) Cumulative release at L/S=10	ANC (mg/kg) Broken aggregate (d <2 mm) L/S=10	Ratio Column/ANC
pH	9.01	9.58	
Al	3.58	2.99	1.20
B	4.47	4.69	0.95
Ca	131	164	0.80
K	7.9	11.1	0.71
Li	0.27	0.29	0.94
Mg	49.0	42.7	1.15
Mo	0.86	0.88	0.98
P	1.98	1.74	1.14
S	106	125	0.85
Si	26.7	24.7	1.08
Sr	0.32	0.35	0.91
Average			0.98
Std			0.15
N			11

Table II. Comparison of log transformed data.

	Log column (mg/kg)	Log pH stat (mg/kg)	Ratio log column/log pH stat
Al	0.554	0.476	1.165
B	0.651	0.671	0.969
Ca	2.117	2.215	0.956
Co	-1.892	-1.699	1.114
Cr	-1.690	-2.095	0.807
Cu	-1.767	-1.843	0.959
Fe	-1.528	-1.572	0.972
K	0.896	1.044	0.858
Li	-0.568	-0.539	1.054
Mg	1.690	1.630	1.037
Mn	-2.645	-2.301	1.149
Mo	-0.067	-0.057	1.175
Na	1.390	1.683	0.826
P	0.297	0.240	1.234
S	2.026	2.097	0.966
Se	-1.114	-0.878	1.270
Si	1.427	1.393	1.024
Sr	-0.497	-0.456	1.090
Zn	-1.906	-1.847	1.032
		Average	1.032
		Std	0.128
		N	19

3.4 Comparison of different leaching test methods

To assess the performance of the compliance leaching tests, as developed in CEN TC 154 Aggregates, a comparison is made between tests on intact pellets and size reduced pellets. The following methods have been applied: column test on intact pellets to quantify the ultimate release at a longer time scale, batch tests using a rollertable on intact pellets for 24 up to 96 hours, pH dependence test on pellets size reduced to < 2 mm and the CEN TC 154 method. The comparison is complicated due to the different end pH in TC 154 method and the other tests. From the column test and batch test up to 96 hours contact time, it can be concluded that very similar results are obtained (table III). These data also correspond well with the equilibrium- based pH stat test data on size reduced pellets (<2 mm) after 24 hours at the same pH as column and batch test. This implies that a similar comparison between TC 154 and pH stat at the corresponding pH could be expected. However, the TC 154 data are in all cases significantly lower than the pH stat data at corresponding pH. For a second type of aggregate, the same has been observed. Apparently, the test conditions as specified in the TC 154 method are not stable as diffusion from the particles is not completed in 24 hours. Since it only takes a few days longer to reach more stable conditions, which would also be more appropriate in relation to assessing environmental impact, two options exist to modify the procedure. Either use a longer contact time for the test or apply size reduction to speed up the process. The ruggedness and reproducibility of the TC 154 test will be negatively affected by the present testing conditions.

Table III.Comparison of size-reduced pellets with intact pellets in different test conditions.

	Aggregate 1					Aggregate 2	
Parameter	Column L/S=10 Intact, pH = 9.3 -8.5	Batch T=96 hrs L/S=10 pH = 9.5	pH stat 24 hrs L/S=10 pH=9.5	pH stat L/S=10 24 hrs pH=8.3	TC 154 24 hrs Intact pH=8.3	pH stat 24 hrs L/S=10 pH=9.5	TC 154 24 hrs Intact pH=9.8
Ba	0.11	0.033	0.035	0.18	0.014	0.91	0.38
Ca	130	125	164	365	55	666	63
K	7.9	10.8	11	19	2.1	30	2.7
PO4 (P)	1.9	0.91	1.7	1.1	0.54	1.6	0.065
SO4 (S)	106	100	124	119	48	144	35
Mo	0.86	0.61	0.88	0.58	0.50	0.079	0.055

3.5 Utilization of aggregates in concrete.

The main intention for use of the aggregate is in the construction of light-weight concrete. The environmental evaluation is based on a scenario approach as described in ENV 12920 [16]. In this application, the leaching process is largely governed by the chemical environment that is imposed by the cement. Based on other work [17], the leaching of metals is hardly an issue in leaching from cement-based products. The main parameters in release from cement-based products are oxyanions, such as Cr VI, V, Mo, and in case of application in drinking water sector Al. A crucial issue for synthetic aggregates, is the extent to which the construction debris resulting from cement-based products containing these synthetic aggregates pose undesired long term effects in leaching after the leaching conditions imposed by the cement are no longer maintained. Recycling of concrete containing synthetic aggregate in new cement-based products will not likely lead to unacceptable release in the service life of such new products. The significant pH change, as a result of the carbonation of the highly alkaline matrix upon degradation or forced size reduction, is important in this respect. The evaluation of cement-based products after their service life in unbound form should be based on size reduced material, which due to the enhanced exposure to the atmosphere is more strongly carbonated and as such has a lower pH than normal cement mortar or concrete. The changes brought about by this combination of effects are covered largely by the pH dependence leach test [5]. The range of leachability conditions that construction debris (including synthetic aggregate) can cover in their "second life" are reflected by the leachability behaviour going from pH 13 (porewater pH of cement) to neutral conditions pH 8 (calcite controlled system). This evaluation is illustrated in Figure 3. In the case of Cr the leachability of the cement aggregate mix (after size reduction to < 2 mm) is clearly dominated by the cement itself as the leaching data for reference mortar and synthetic aggregate mortar coincide (Cr leaching from aggregate is low). In the case of Mo, the leaching behaviour of crushed synthetic aggregate mortar is changed after incorporation in cement. Here the aggregate does increase the release level over that imposed by the cement itself. The data as obtained for size reduced material exceed the present regulatory limits for construction materials in the "end of life" stage. The size range of construction debris can range from very coarse material (to be judged rather as a monolith) to fine material, which is best judged as a granular material. Here the latter is chosen, which is a worst case approach. Work to assess the intermediate particle size ranges and their contribution to the overall leaching process is underway.

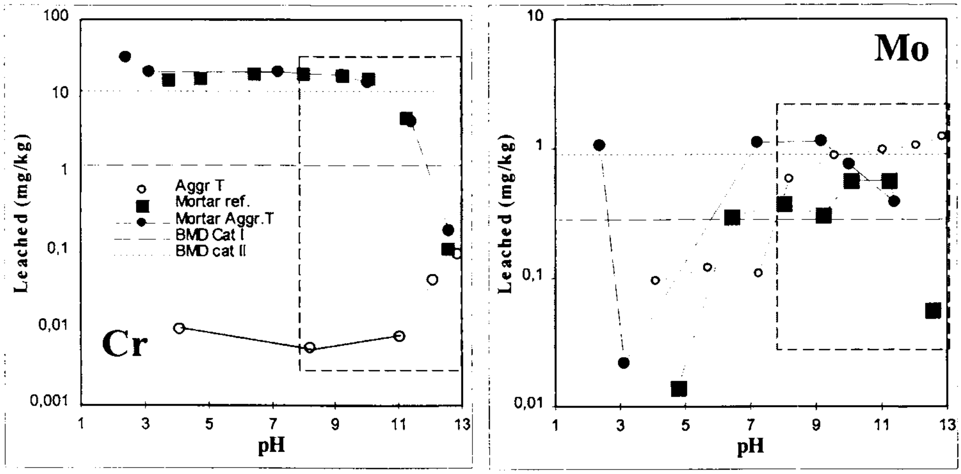

Figure 3. Leaching data for crushed synthetic aggregate mortar in comparison with the leaching behaviour of the synthetic aggregate. BMD = Building Materials Decree [10]. The relevant pH window is given as a box.

4. CONCLUSIONS

When waste leachability is compared with leaching data on synthetic aggregates produced from mixtures of wastes, generally significantly lower leachability is observed for many constituents.

Due to the quite low acid neutralization capacity, the sensitivity of aggregates to external pH influences is considerable. When the aggregate is used in concrete for gravel replacement, this property has no further consequences. When used in contact with acidic environments, however, undesired leaching might occur.

The leaching curves as a function of pH are very consistent, which can be regarded as a characteristic for synthetic aggregate. Apparently, the process characteristics tend to produce a material with similar properties in spite of varying inputs. This can be used for QC of the production process with a concise test addressed the most crucial leaching aspects.

In a comparison of the release at LS=10 for the column test on 10 mm pellets with the same material broken to less than 2 mm at the corresponding pH at LS=10 in the pH dependence test, no significant difference is noted for almost all elements. By applying a log transformation, it is clear that the agreement even extends to the elements leached in low concentrations.

The test conditions as specified in the CEN TC 154 method are not stable as diffusion from the particles is not completed in 24 hours. The inherent instability, which is most pronounced for pellets with moderate to high porosity, can be avoided by applying a longer contact time for the test or by applying size reduction.

Upon application of synthetic aggregates in cement-bound products, the effect of the aggregate leachability is generally suppressed, except for Mo that shows a mild increased leachability of the final product. The main issue for aggregate use in concrete is to ensure that its behaviour in the recycling and end of life stage does not adversely affect the long term leaching behaviour of cement products.

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Waste Materials in Construction
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Leaching of heavy metals from soils – an analysis

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The leachabilities for As, Cd, Cr, Cu, Hg, Pb, Ni, Zn of ca. 1000 lots of (untreated and treated) soils have been measured. The leachabilities are largely independent on concentration over a broad concentration range. From an evaluation against legal leaching standards, a decision support system is derived. Thermal treatment and soil washing generally yield an improved soil quality in terms of leachability.

1. INTRODUCTION

In The Netherlands, the use of secondary materials, in civil engineering works, is regulated by the Dutch Act for Building Materials (Bouwstoffenbesluit) [1], which came into effect in July 1999. An overview of the Dutch soil classification scheme is given in Figure 1.

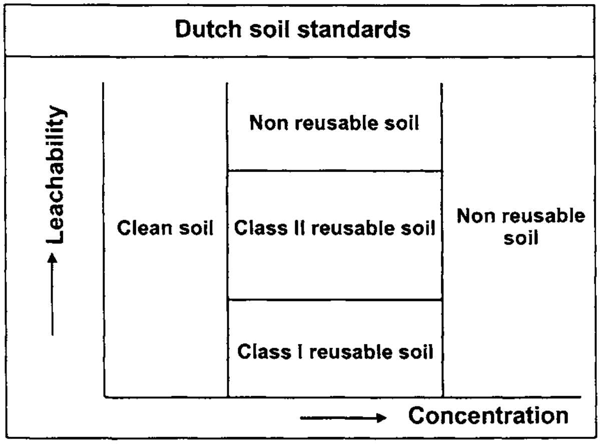

Figure 1. Dutch soil classification scheme

For the application of mildly contaminated soils, both untreated and treated, this encompasses the following rules:

- Limit concentration values for organic contaminants.
- Limit concentration values for inorganic and heavy metal contaminants. The height of application is determined by the leachability, as is depicted in Figure 2. Class I soil can be applied without any particular measures. Class II soil can only be applied when measures to prevent leaching to the surrounding environment have been taken.

It is compulsory to determine the leachability of inorganic contaminants and heavy metals by the standard L/S=10 column test (NEN 7343). A major drawback of this test is the duration, which is in the order of 4-5 weeks. Especially for soils which originate from construction and building sites, holding times longer than 2-3 days interfere heavily with the logistics of handling, transport and reutilisation. Hence, a clear need exists for fast testing procedures.

In a previous paper by Heynen et al [2] alternative fast leaching tests have been investigated. Both a short L/S=1 column test (NEN 7343) and a 2-step L/S=10 batch test (CEN TC 292) correlate positively with the L/S=10 column test (NEN 7343). However, because of the relatively large correlation bandwidth between the various tests, practical application is not feasible. This paper also indicates that, within a certain bandwidth, heavy metal leachability is largely independent on concentration over a broad concentration range. This paper expands on this latter observation in an attempt to define a decision support system to predict leachability values based upon concentration values only.

A giant database has been compiled, consisting of leachability data for 8 metals, from organisations active in soil reuse and recycling. These organisations include: Grond- en Reststoffenbank Rotterdam, Grondbank Amsterdam, Grondbankcombinatie and the Centre for Soil Treatment. This paper discusses an analysis of this database.

2. METHODS AND MATERIALS

All chemical (concentration) and physical (pH, lutum, fraction < 63 μm, organic matter) analyses and the L/S=10 column test (NEN 7343) were performed under Dutch standard norms or with validated methods proven to be equivalent to these norms.

The following soils were selected:

- 420 lots of untreated soils, originating from building and construction sites. These types of soils range from sandy to clayey.
- 126 lots of soil, originating from soil washing plants. These soils are sandy.
- 444 lots of soils, originating from thermal treatment plants. These types of soils range from sandy to clayey.

For all soils the heavy metal concentrations fall within the (reuse) concentration limits as imposed by the Dutch Act for Building Materials. A description of the principles and practice of soil washing and thermal treatment are given elsewhere [3-5].

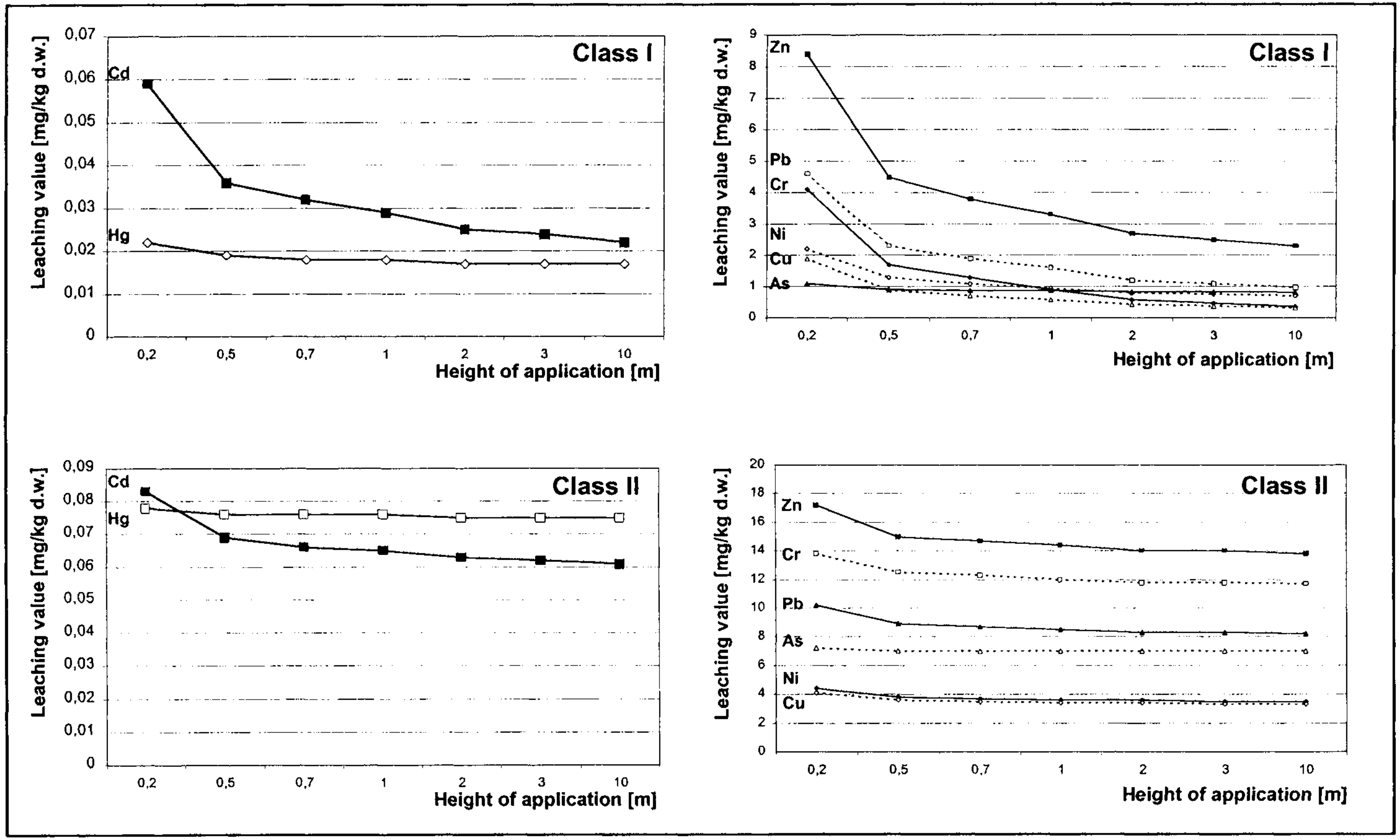

Figure 2. Class I and II leaching standards according to the Dutch Act for Building materials

3. RESULTS

In Figures 3-6 are depicted the (measured) leachabilities for untreated and treated soils. In all Figures the continuous lines represent the Class I leaching standard for an application height of 2 m. The dashed lines represent the average leachability. In Table 1, the chance of exceeding the Class I leaching standards, for all soil types and 8 heavy metals, is given. For Figures 3-6 and Table 1, the (few) data for soils with a pH lower than 5 have been omitted from our analysis, since application of these type of soils always requires carrying out the standard L/S=10 column test [2].

Table 1.
Percentages of leachability data exceeding the Class I leaching standard as a function of height (h) of application. N = total number of data. Average, Minimum and Maximum leachability are expressed in mg/kg d.w.

					a) untreated soil						
	N	Ave.	Min.	Max.	h=0,2 m	h=0,5 m	h=0,7 m	h=1,0 m	h=2,0 m	h=5,0 m	h=10,0 m
As	44	0,12	0,01	0,4	0%	0%	0%	0%	0%	0%	0%
Cd	100	0,010	0,0001	0,4	2%	2%	2%	2%	2%	2%	2%
Cr	12	0,036	0,005	0,1	0%	0%	0%	0%	0%	0%	0%
Cu	105	0,33	0,006	2,5	2%	5%	11%	16%	24%	30%	33%
Hg	383	0,0038	0,0001	0,2	2%	2%	2%	2%	2%	2%	2%
Pb	169	0,43	0,001	5,7	1%	2%	4%	5%	8%	11%	11%
Ni	18	0,0797	0,012	0.21	0%	0%	0%	0%	0%	0%	0%
Zn	232	0,70	0,001	7	0%	1%	2%	2%	3%	3%	3%
Lot	420	-	-	-	2%	3%	5%	7%	9%	11%	12%

					b) washed soil						
	N	Ave.	Min.	Max.	h=0,2 m	h=0,5 m	h=0,7 m	h=1,0 m	h=2,0 m	h=5,0 m	h=10,0 m
As	10	0,12	0,026	0,40	0%	0%	0%	0%	0%	0%	0%
Cd	39	0,005	0,0001	0,019	0%	0%	0%	0%	0%	0%	0%
Cr	9	0,052	0,014	0,13	0%	0%	0%	0%	0%	0%	0%
Cu	96	0,16	0,009	0,80	0%	0%	1%	2%	4%	9%	10%
Hg	39	0,0033	0,0001	0,03	5%	5%	5%	5%	5%	5%	5%
Pb	76	0,094	0,0004	1,0	0%	0%	0%	0%	0%	0%	1%
Ni	25	0,080	0,001	0,58	0%	0%	0%	0%	0%	0%	0%
Zn	96	0,32	0,01	2,5	0%	0%	0%	0%	0%	1%	2%
Lot	126	-	-	-	3%	3%	3%	4%	6%	10%	13%

					c) thermally treated soil						
	N	Ave.	Min.	Max.	h=0,2 m	h=0,5 m	h=0,7 m	h=1,0 m	h=2,0 m	h=5,0 m	h=10,0 m
As	13	0,30	0,0243	1,168	8%	8%	8%	8%	8%	15%	15%
Cd	193	0,0029	0,0001	0,011	0%	0%	0%	0%	0%	0%	0%
Cr	12	0,060	0,018	0,18	0%	0%	0%	0%	0%	0%	0%
Cu	386	0,064	0,0015	3,6	1%	1%	1%	1%	1%	1%	1%
Hg	154	0,0009	0,0001	0,04	1%	1%	1%	1%	1%	1%	1%
Pb	389	0,061	0,001	4,2	0%	0%	0%	0%	0%	0%	1%
Ni	288	0,028	0,01	0,19	0%	0%	0%	0%	0%	0%	0%
Zn	424	0,15	0,0006	3,5	0%	0%	0%	0%	0%	0%	0%
Lot	444	-	-	-	1%	2%	2%	2%	2%	2%	2%

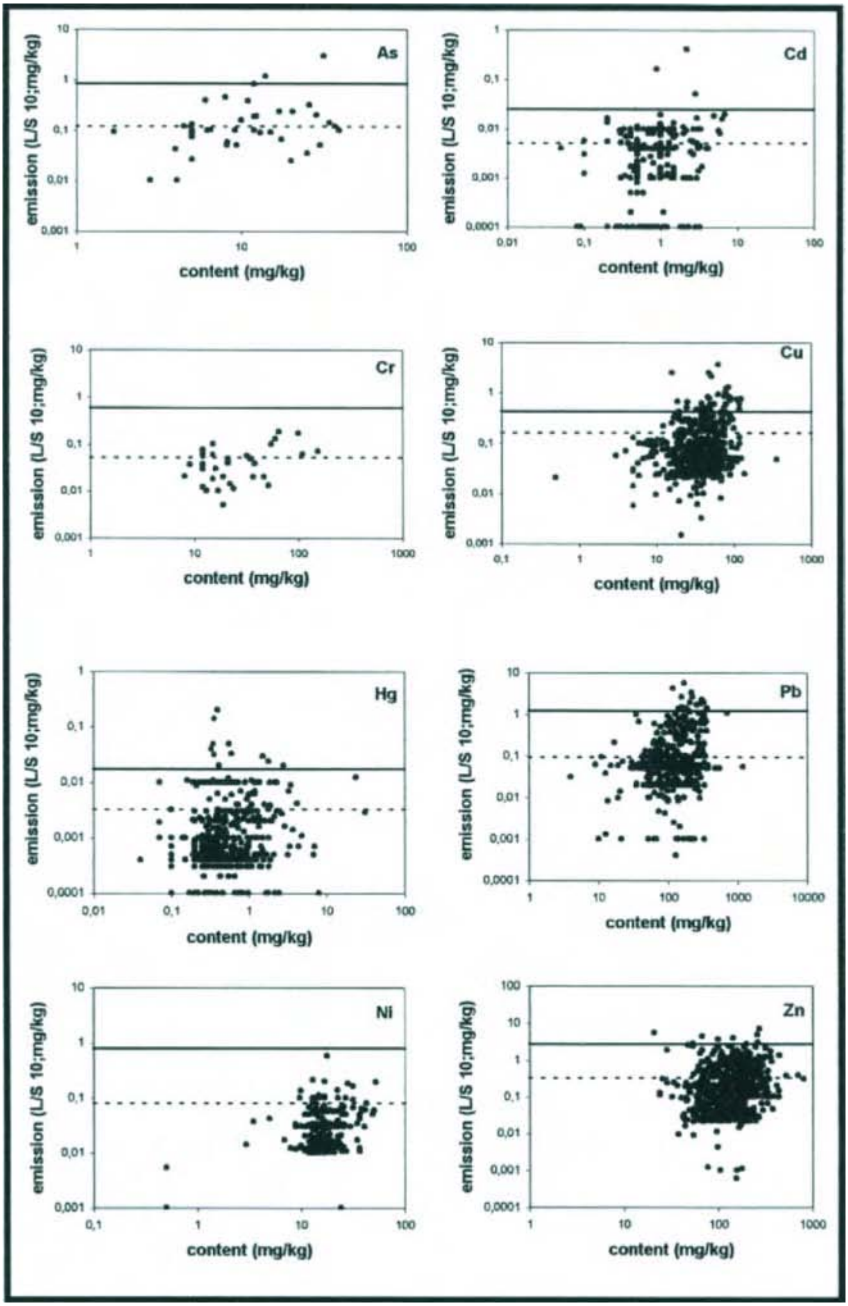

Figure 3. Dependence of leachability on total content for all soils

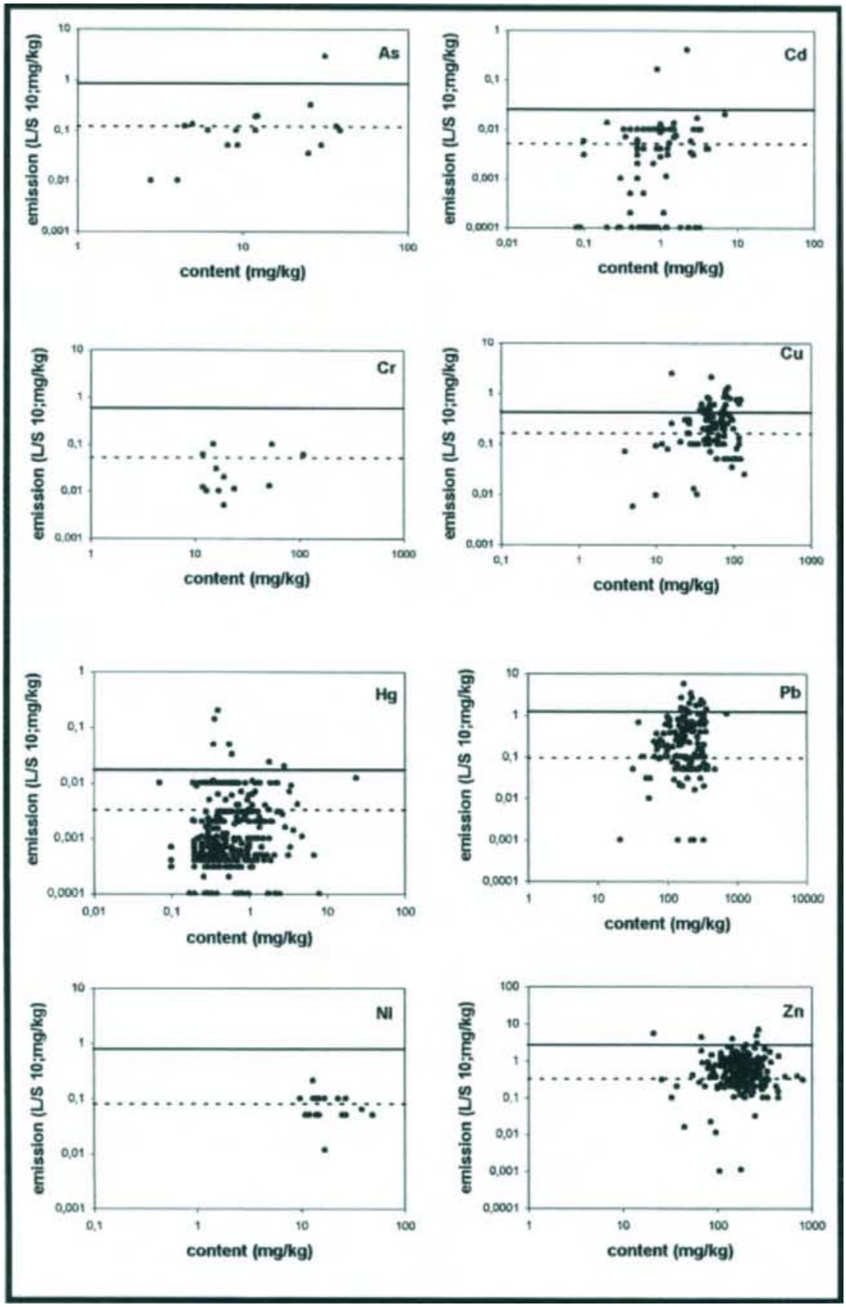

Figure 4. Dependence of leachability on total content for untreated soils

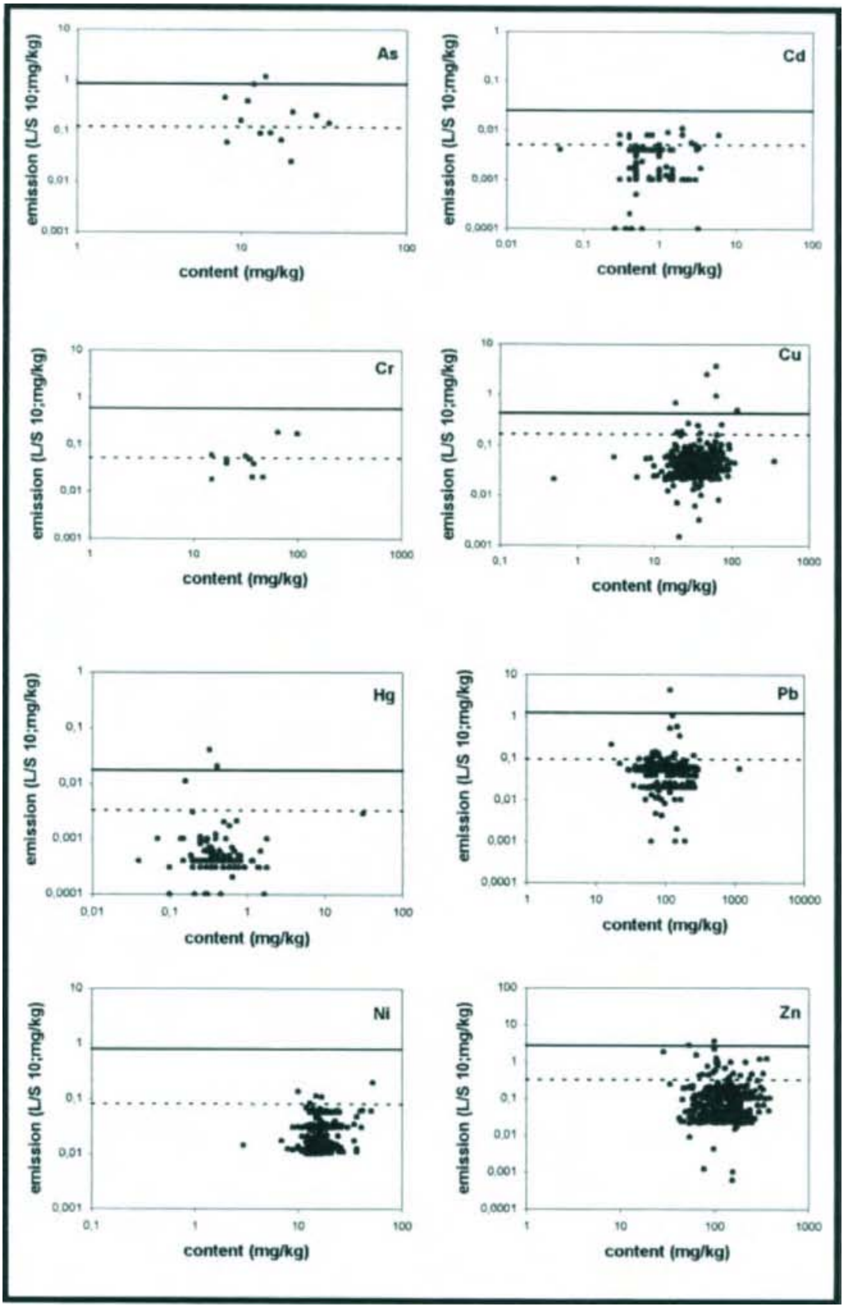

Figure 5. Dependence of leachability on total content for thermally treated soils

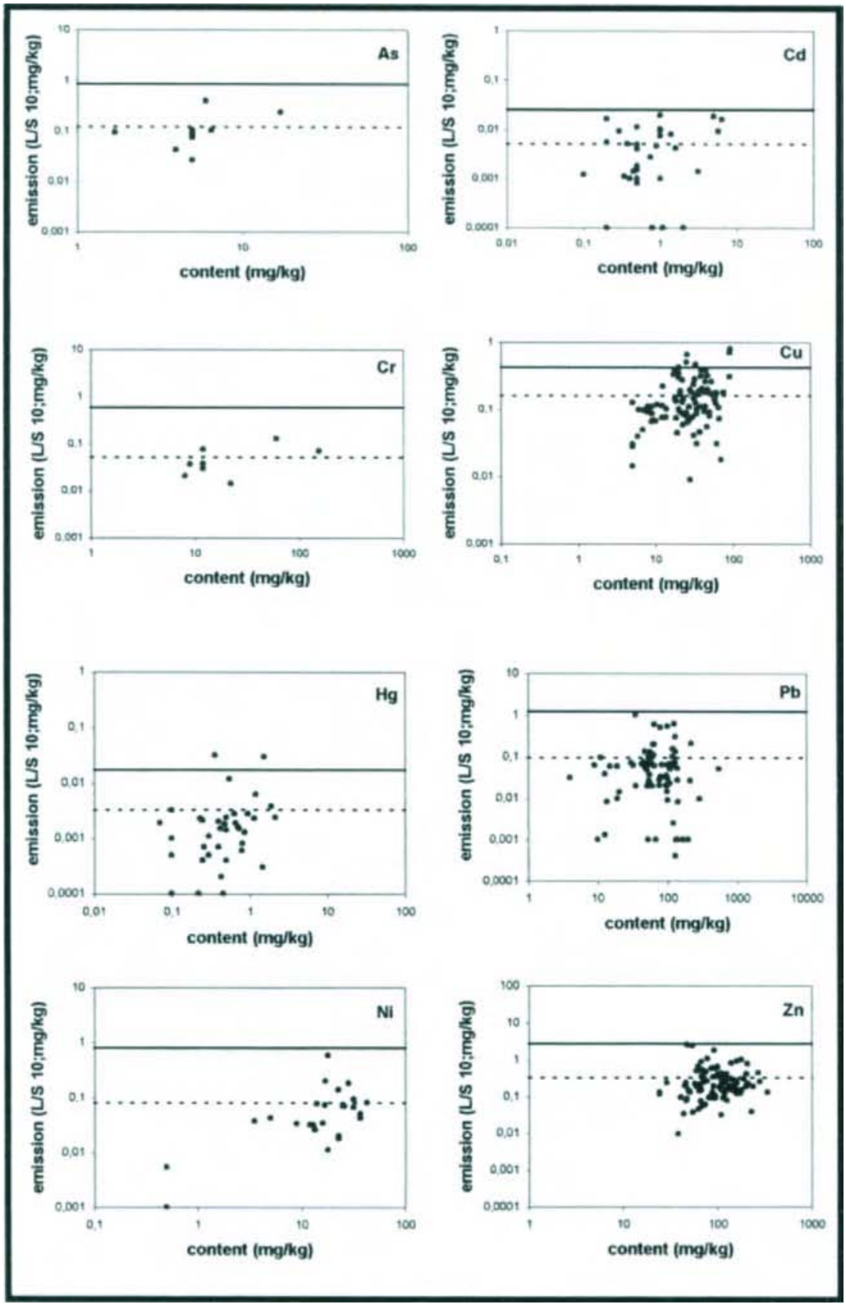

Figure 6. Dependence of leachability on total content for washed soils

4. DISCUSSION

Our observations confirm the findings of Heynen et al. Leachabilities are largely independent on concentration. Accepting a maximum chance of 10 %, per heavy metal, for exceeding the Class I leaching standards, the following rules of thumb apply:

- No leachability tests are required for washed soils, for application heights up to 10 m.
- No leachability tests are required for thermally treated soils, for application heights up to 10 m, provided no arsenic is present. When arsenic is present, application up to 2 m can be tolerated without leaching tests.
- For untreated soils, no leaching tests are required for application heights up to 10 m, provided no copper is present. When copper is present, application up to 0.7 m can be tolerated without leaching tests.
- In all other cases - Class II application, other heavy metals, pH < 5 - leaching tests are compulsory.

The above formulated rules will be proposed to the authorities as legal evidence for application of these soils without leaching tests.

In addition, we attempted to correlate leachabilities with soil physical parameters. No significant correlations could be defined. In Table 2 the average leachabilites for the 3 soil types are given.

Table 2.
Average leachabilities in mg/kg dw.

	Untreated	Wet treated	Thermally treated
As	0.12	0.12	0.30
Cd	0.010	0.005	0.0029
Cr	0.036	0.052	0.060
Cu	0.33	0.16	0.064
Hg	0.0038	0.0033	0.0009
Pb	0.43	0.094	0.061
Ni	0.0797	0.080	0.028
Zn	0.70	0.32	0.15

From Table 2 it is inferred that, for all metals except arsenic and chromium, thermal soil treatment results in an improved soil quality in terms of leachablility. This is in line with the findings of Zevenbergen et al [6]. For cadmium, copper, lead and zinc soil washing seems to yield an improved soil quality.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

The development of a code of practice for the environmental sound use of PFA as a fill

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Although pulverised fuel ash (PFA) has been successfully used in a range of applications for many years there has always been need to give consideration to its environmental impact. The increasing awareness of environmental issues has had an impact on sales, with the need to assess its use on a site by site basis, the time taken to get approval for the use of PFA can exceed the time scales imposed by site operations. There has therefore been a need for an alternative approach to the problem.

This paper details the approach at present being developed. This is a three-stage one with an initial assessment of the process, a review of existing data and what further data is required and finally a code of practice that recommends a rational approach to the use of PFA as a fill.

1. INTRODUCTION

There is a proposal for codes of practice for the use of recycled materials to minimise the impact of their use on the environment. A three stage process, has been suggested, the first being a review of the current knowledge. This paper reviews the current practice when using PFA as a fill material. The environmental impact of the different activities are assessed and related to the environmental information currently available. The aim is to highlight suitable practices for using PFA as a fill and the testing that is required to categorise it.

2. CURRENT PRACTICE

The first stage in the development of a code of practice is to review the current practice to identify the issues that need to be addressed.

2.1. Production

PFA (also known as fly ash in many countries) is a by-product from the combustion of pulverised hard coal in electricity power generation. It is a fine powder, similar in fineness to cement, which consists mainly of oxides of silica, alumina, iron, calcium and various minor constituents. This section identifies the potential environmental problems associated with the use of PFA as a fill material.

2.2. Recovery of PFA from stockpiles.

The recovery process involves exposing an area of stockpile, which is then excavated and loaded into wagons. There is clear potential for dust blow from the exposed face as well as in the handling process. Additionally the removal of some material on the wheels and bodies of the lorries, which may get deposited on the roads, can be a problem. Items such as spillage of diesel and tramp materials need to be considered at the design stage for the PFA stockpile but this is not considered within the code of practice for fill.

2.3. PFA from Lagoons

Similar considerations apply to lagoons as with stockpiles. There may be a greater tendency for the wetter material to adhere to vehicles.

2.4. Conditioned PFA

It is essential that mixers that are used to condition the material i.e. moisten the PFA, are designed in such a way to prevent fugitive dust from being emitted from them. Consideration needs to be given to methods of cleaning mixers and disposal of the waste as well as the material deposited on the ground around the loading point.

For all the above categories of PFA, should a vehicle be overloaded, a properly managed procedure for tipping off any excess material is required.

2.5. Transport

Major problems are associated with dust blow from unprotected wagons and deposition of materials on public roads from the body of the wagon.

2.6. Design

Account must be taken of the environmental impact of the construction in the design process. This will involve ensuring that there is an adequate drainage layer to prevent capillary rise and saturation of the PFA. Additionally the profile of the PFA should be such to allow efficient run off of rainwater both during and after the construction period. Long-term protection of any side slopes is required to prevent build up of run off and any potential leaching problems. Suitable methods of encouraging the growth of plants and trees or physical barriers must be designed into the structure.

2.7. Laying and Compaction

The primary considerations when placing PFA is one of minimising dust blow by ensuring that PFA as delivered and after compaction is maintained sufficiently moist to prevent dust being created. Windy conditions result in the greatest risk of the PFA being dried out. Therefore, water-spraying equipment is recommended to remoisten the surface. PFA, which has been accidentally over moistened, can be allowed to dry out by breaking up the surface to encourage evaporation. After a suitable period of time the PFA may be reused when the optimum moisture content is achieved. Alternatively dry PFA can be blended into the wet material.

If material is stockpiled on site it should be deposited in such a way as to prevent accidental contamination of adjacent watercourses. Vehicles leaving the site need to be in a clean condition and provision of wheel washers or similar may be required.

2.8. Summary – Current Practice

The main environmental risks associated with the process of using PFA as a fill material are primarily ones of common sense when working with fine powders. That is:

- Prevent contamination of adjacent watercourses.
- Prevent dust problems by keeping the material moist.
- Protect the material from wash out by profiling, establishing vegetation, physical barriers or reducing trafficking.

3. ENVIRONMENTAL ASPECTS OF PFA

3.1. Physical Properties - Particle Size and shape

As a consequence of the way they are produced, PFA particles, particularly those below 50 vm, are spherical in shape. As the coal is burnt, the minerals associated with it become molten and form the spherical shape. Because of the rapid cooling experienced by the fine ash particles as they pass out of the furnace, they solidify as an amorphous, glassy material in this shape.

PFA is predominantly silt/fine sand in size and have potential to become airborne in certain conditions. The particle size also means that compacted PFA has a low permeability, typically 10^{-7} m/s. This means that it is difficult for water to penetrate and because water will only flow through saturated material, this will not occur unless the PFA is placed in areas below water. Experience has shown that if PFA is subjected to heavy rain it is unusual for saturation to affect the surface beyond the top 50 mm. Even when saturated there will only be a limited rate of flow through the mass of the material.

Table A – Solid phase trace element analysis

	Typical range of results for UK sources (mg/kg)
Arsenic	4 to 109
Boron	5 to 310
Barium	0 to 36,000
Cadmium	<1.0* to 4
Chloride	0 to 2,990
Cobalt	2 to 115
Chromium	97 to 192
Copper	119 to 474
Fluoride	0 to 200
Mercury	<0.01* to 0.61
Manganese	103 to 1,555
Molybdenum	3 to 81
Nickel	108 to 583
Phosphorus	372 to 2,818
Lead	<1* to 976
Antimony	1 to 325
Selenium	4 to 162
Tin	933 to 1,847
Vanadium	292 to 1,339
Zinc	148 to 918

* Indicates below the limit of detection

3.2. Chemistry

Around 60 % to 90 % of PFA is present as an amorphous glassy material composed of oxides of silicon, aluminium and iron. Other metals are present in smaller quantities. Apart from the glass, the constituents with most influence on the properties of PFA are the calcium oxide content (lime) and sulfate content.

When water is added to PFA it initially has a low pH as the sulfate deposited on the surface of the particles is brought into solution as a weak sulfuric acid. This is a transient situation and the pH rapidly rises as calcium is leached into solution. The pH of leachate is typically 8 to 11 but may be as high as 12.

The calcium content of PFA means that most of the sulfate is present as gypsum, which has a limited solubility and will precipitate out in compacted PFA. The sulfate level of lagoon PFA is usually very low because the water/solids ratio used to slurry the PFA means the majority of the sulfate is washed out. Other water-soluble materials are also removed in the process. The sulfate content is typically less than 0.1 g/L and the pH is usually around 9.

3.3. Trace Elements

Typical trace elemental analyses are shown in Table A, which demonstrates that other elements are present in only small quantities, less than 1 % of the total. The values quoted are generally in agreement with other quoted values.[1,2]

3.4. DIN Leaching test

As discussed above, there is only a small fraction of the constituents that are present on the surface of PFA and that are leachable in water. Typical data obtained from routine analyses are shown in Table B, the extraction in this instance is to the German standard DIN 38414-S4[3] (10:1 water/solids ratio).

From the data it can be seen that the major water-soluble constituents are calcium and sulfur (usually present as sulfate). There are smaller amounts of sodium and potassium, and traces of chloride, magnesium, aluminium and silicon. If it is assumed that all the water soluble calcium, sodium and potassium is present as hydroxide (ignoring the sulfate or chloride) then the total water soluble hydroxide, based on the highest values from Table B would be 2.1% (m/m). However, calcium hydroxide would make up approximately 2.0%, the others would represent less than 0.1 %. In all instances quoted the calcium is very dominant with sodium and potassium present in very small quantities in comparison.

3.5. Harwell Test

Samples[4] of stockpile PFA were subjected to extraction by the Harwell[5] method and the results are summarised in Table C. Although it is stockpile PFA the leachate still shows that the calcium content is dominant, with lesser amounts of other elements. There is a more significant amount of magnesium, probably due to the low pH of these samples.

The CIRIA report[6] compared the CEN two-stage leaching method to the Harwell method. It demonstrated that the total leachate was similar for both techniques for the three PFA's examined. Both showed that with the Harwell method the calcium and sulfate were present either in the ranges 100 to 1000mg/L or 1000 to 10000 mg/L for the first bed volume extracted but fell to the 100 to 1000 mg/L range for the next four bed volumes extracted.

The concentration for the 6-10th bed volumes fell to 10 – 100 mg/L. The only other elements that were present in these levels were sodium and potassium, but these had significantly reduced by the third bed volume for all but one of the PFA's examined.

Table B – Leachates found using the DIN 38414-S4 method.

Typical range of leachable elements for UK PFA (mg/L except pH)			
Aluminium	<0.1* to 9.8	Manganese	<0.1*
Arsenic	<0.1*	Molybdenum	<0.1* to 0.6
Boron	<0.1* to 6	Sodium	12 to 33
Barium	0.2 to 0.4	Nickel	<0.1*
Calcium	15 to 216	Phosphorus	<0.1* to 0.4
Cadmium	<0.1*	Lead	<0.2*
Chloride	1.6 to 17.5	Sulfur	24 to 510
Cobalt	<0.1*	Antimony	<0.01*
Chromium	<0.1*	Selenium	<0.01* to 0.15
Copper	<0.1*	Silicon	0.5 to 1.5
Fluoride	0.2 to 2.3	Tin	<0.1*
Iron	<0.1*	Titanium	<0.1*
Mercury	<0.01*	Vanadium	<0.1* to 0.5
Potassium	1 to 19	Zinc	<0.1*
Magnesium	<0.1* to 3.9	pH	7 to 11.7

Notes: * Indicates below detection limit

The above data include a seawater-conditioned sample, hence the high chloride values

3.6. Leachates - Summary

- The majority of the ash is present as an alumino-silicate glass;
- Most elements are present in very small quantities and are largely entrained in the glassy material;
- Typically less than 2 % of the PFA is water-soluble; calcium and sulfate constitute the majority of the water-soluble fraction. There are smaller amounts of sodium, potassium and, in low pH leachate, magnesium;
- The pH is mainly determined by the water-soluble calcium and sulfate;
- The water-soluble fraction, though small, can be sufficient to produce a pH above 11.5, but dilution can rapidly reduce the water-soluble fraction and therefore the pH.

3.7. Dust suppression

Avoid creating airborne dust wherever possible. Where dust is generated then engineering control measures should be considered (water sprays) to maintain the airborne dust concentration as low as is reasonably practical. Movement of traffic over the material should be reduced to a minimum.

4. SUMMARY AND CONCLUSION

It has been established that the leachate is small and consists mainly of calcium sulfate. There are only very small amounts of other elements available to leach, the most significant being boron because of its potential problems with plant growth. However, these can be overcome by selection of boron tolerant plants for growth in PFA. Furthermore, there is little significant difference in leachate quality between all UK PFA's, and these are well established. The major exception is lagoon PFA that will have lower leachate content. Therefore only limited testing is required to demonstrate consistency of the leachate, although if there is any major change in fuel burnt then there will be a need to demonstrate that there is no effect on leachate quality.

Table C – Leachates found using Harwell method.

Typical range of leachable elements, 10 samples, single source (mg/L except pH)			
Bed Volume	1	Molybdenum	0.15 to 0.88
PH	8.1 –8.8	Sodium	5 to 44
Aluminium	<0.1* to 0.5	Nickel	<0.01*
Arsenic	0.06 to 0.16	Lead	<0.01*
Boron	1.8 to 4.3	Tin	<0.01*
Calcium	33 to 250	Titanium	<0.01*
Cadmium	<0.005*	Vanadium	0.22 to 0.55
Cobalt	<0.01*	Zinc	<0.01*
Chromium	0.02 to 0.06	Nitrogen	0.2 to 1
Copper	<0.01*	Phosphorus	<0.1*
Iron	<0.01*	Sulfur	15 to 70
Mercury	<0.001*	Chloride	5 to 9
Potassium	5 to 29	Fluoride	<0.1*
Magnesium	16 to 100	Selenium	0.04 to 0.16
Manganese	<0.01*	Antimony	<0.2

*Indicates value below detection limit

The typical construction of an embankment is to place a drainage layer beneath the PFA to prevent capillary rise, to protect the side slopes with topsoil and/or vegetation and to build the road on top. In such situations the PFA is effectively isolated from the surrounding environment and therefore does not present a risk with regard to pollution. The major risk of water ingress would be from cracked surfacing, but this would be for a limited period of time and the effect would be small due to the impermeability of the PFA. Thus if such structures are to be built there is no need for a major impact assessment other than establishing that the fuel burn, and therefore leachate potential of the PFA, is consistent and provide a method statement for handling the material on site. The method statement should cover measures to prevent accidental discharge into watercourses and prevent dust blow.

In other types of fill structures, where the PFA cannot be protected to the same extent then an environmental impact assessment will be required. This should take into account the low permeability of the PFA. There is again no need for significant amounts of testing provided the producer can demonstrate the consistency of the leachate potential.

If monitoring of the PFA is required for any reason then the nature of the monitoring needs to be established. Both conductivity and pH measurement can be readily measured.

The findings above can be summarised as detailed below.

- It can be shown there are no known problems with leachate, e.g. small amounts and low permeability
- All UK sources appear similar.
- No known problems of leachates causing environmental problems.

Therefore the following procedures are recommended:

- Monitor leachates using an approved method from each source annually to ensure consistency of material.
- No further testing should be required unless there is a major change in fuel type.
- If PFA is to be used within an area deemed to be environmentally sensitive area then conductivity and pH monitoring can be carried out at the rate agreed between the customer and the supplier.

5. FURTHER WORK

Although there are no known major problems associated with the use of PFA as a fill material there is a need to establish the effects of large fill projects where the PFA cannot be fully isolated from the environment. This would enable more focussed assessments to be made.

6. DEVELOPMENT AND USE OF THE CODE OF PRACTICE

The Code of Practice will be produced based on the information above and will be available to provide a framework for the design engineers to follow to ensure that a proper assessment is made of the possible effects on the environment. This should ease the amount of work required by the environmental bodies in deciding the suitability of PFA in a given scheme.

To ensure confidence in the Code of Practice, during its development the UKQAA will work closely with the Environment Agency.

As stated earlier, there will be changes in the knowledge base and thus it is envisaged that the code will be updated from time to time to take account of this. Again, any changes will be made with input from the Environment Agency.

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G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Leaching behaviours of heavy metals from MSWI residues and Pb adsorption onto the residues under alkaline condition

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A small-scale column test simulating a monofill landfill site, which is composed of MSWI residues alone, was performed. The pH of the leachate was higher than 12 for 2 months and the adsorption of Pb and Zn onto the residues took place. The Pb adsorption was Freundlich type, based on batch experiments to study adsorption behaviour. Adsorptive ability of MSWI residues were different for each residues, and a positive correlation between adsorptive ability and total contents of "Fe + Si + Mn + Al" of MSWI residues was observed.

1. Introduction

More than 1800 municipal solid waste incinerators (MSWI) exist and about 6.2 million tons of MSWI residue is annually generated in Japan [1]. Almost all of MSWI bottom ash is landfilled directly while most of fly ash (a mixture of "fly ash" and "air pollution control residue" is termed "fly ash" in Japan) is landfilled after proper treatment. Most of MSWI residues are strongly alkaline. The leachate from these alkaline residues measured using JLT-13, according to Notification of No.13 of Japanese Environment Agency, which is a single batch type leaching test using distilled water as a leachant, often shows high pH (more than 12) and Pb leaches in high concentration [2]. The pH change and leaching behaviour of MSWI residues in the environment, including adsorption of metals, are important in safety management and reuse of MSWI residues. Therefore small-scale column experiments simulating monofill disposal sites and batch experiments to study Pb adsorption behaviour onto the residues were performed in this study.

2. Experiment

2.1. Samples

Three kinds of MSWI residues, two kinds of fly ash (Fly ash A, Fly ash B) and one bottom ash sample collected from stoker type MSW incinerators in Japan, were used. Fly ash A was derived from an electrostatic precipitator and fly ash B was derived from a fabric filter. Both fly ash contained slaked lime ($Ca(OH)_2$) as the acid gas treatment system is a dry system. Bottom ash was derived from another stoker type incinerator, and was collected immediately after quenching. All the residues were stored under air tight conditions. Element contents and JLT-13 results are shown in Table 1.

Table 1
Element contents and leaching test (JLT-13) results of samples

	Fly ash A	Fly ash B	Bottom ash
	Contents of element (mg/kg)		
Ca	207,000	366,400	130,000
Fe	6,190	3,020	2,590
Al	78,600	18,700	58,800
Na	28,550	23,440	18,500
K	37,470	32,600	10,800
Cl	94,000	76,200	8,570
Pb	1,370	1,920	240
Cd	73.5	76.1	14.7
Cu	570	410	2,550
Zn	6,010	5,470	4,020
	Results of JLT-13 (mg/L except pH)		
pH	12.6	12.7	12.4
Pb	5.2	23.6	<0.05
Cd	<0.01	<0.01	<0.01
Cu	2.2	0.13	0.95
Zn	31.6	7.48	<0.05

2.2. Experiment method

2.2.1. Experiment 1 A small-scale column test simulating a monofill landfill site

In order to understand the pH change and behaviour of metals in leachate, a small scale column test simulating a monofill landfill site were performed. Two acrylic cylindrical columns (diameter = 50 mm and height = 500mm) were prepared. They were filled with 450g of mixture of fly ash A and bottom ash at a ratio of 1:4 (weight) of the thickness of 200mm (filling density = 1.15 g/cm^3), with glasswool of the thickness of 10mm and with glass bead of 200 mm thick whose particle diameter was 5 mm. A rubber cap was set at the bottom of the column. As a leachant, nitric acid (pH 4) and the leachate of the fly ash B (JLT-13, pH and leaching concentration are referred to Table 1) were used in order to simulate a possible fluid in landfill sites, that is acid rain and leachate of MSWI residues. From the top of the column they were poured at a velocity of 9.8 mL/h for 7.6 h (= 74.5 mL) once a week, which is based on the average rainfall of 2000 mm/year in Japan. The leachate which passed through the glass bead was directed to the Erlenmeyer flask. The equipment setup is shown in Fig. 1. The leachate in the Erlenmeyer flask was analyzed of the next day.

2.2.2. Experiment 2 Batch test to study Pb adsorption onto MSWI residue

1g or 10 g of each residues with 100mL distilled water were poured into 8 polyethylene bottles (250mL). The bottles were agitated for 6 hours under JLT-13 conditions. The leachate of 4 bottles of them were vacuum filtrated with a glass fiber filter paper (diameter = 1 μm). 0, 2, 4, 6 mg of Pb in the form of lead nitrate ($Pb(NO_3)_2$), a standard solution for atomic adsorption spectrometry whereby the Pb concentration is 10000 mg/L, were added to the solution. These correspond to 0, 20, 40, 60 mg/L of soluble Pb concentration respectively. After addition of Pb, the samples were agitated again for 1 hour and vacuum filtrated. These samples were named "Sample series No.1 (without fly ash)". The remaining 4 samples were agitated for 1 hour after addition of 0, 2, 4, 6 mg of Pb without filtration. Samples after filtration were named "Sample series No.2 (with fly ash)". Pb in the solution of both samples

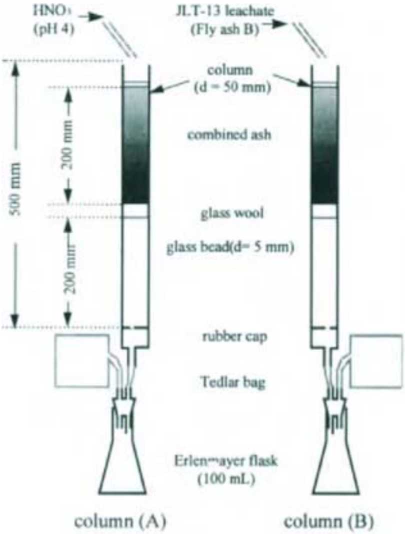


Figure 1. Equipment for column experiment test

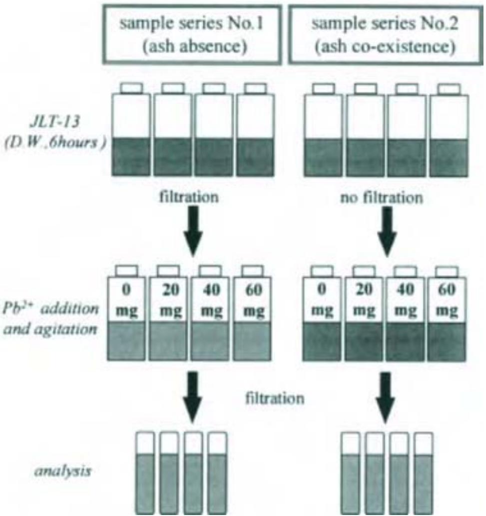


Figure 2. Experiment scheme for adsorption

was determined by inductively coupled plasma spectrometry (Seiko SPS-1500VR) after measuring of pH, ORP, temperature. This experiment scheme is illustrated in Fig. 2.

3. Results and discussion

Time courses of the quantity of leachate and pH of the leachate are shown in Fig. 3 and Fig. 4. In the first leaching step, an outflow as the leachate is only 67 % of an inflow as the leachant.

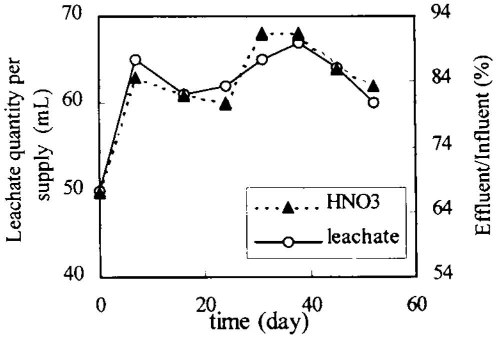


Figure 3. Time course of leachate quantity per supply

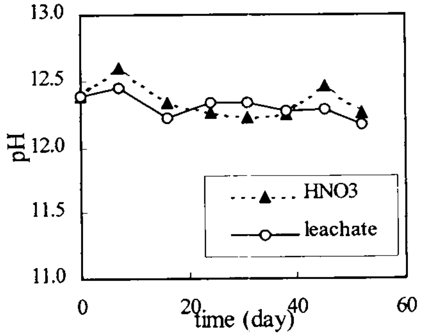


Figure 4. Time course of leachate pH

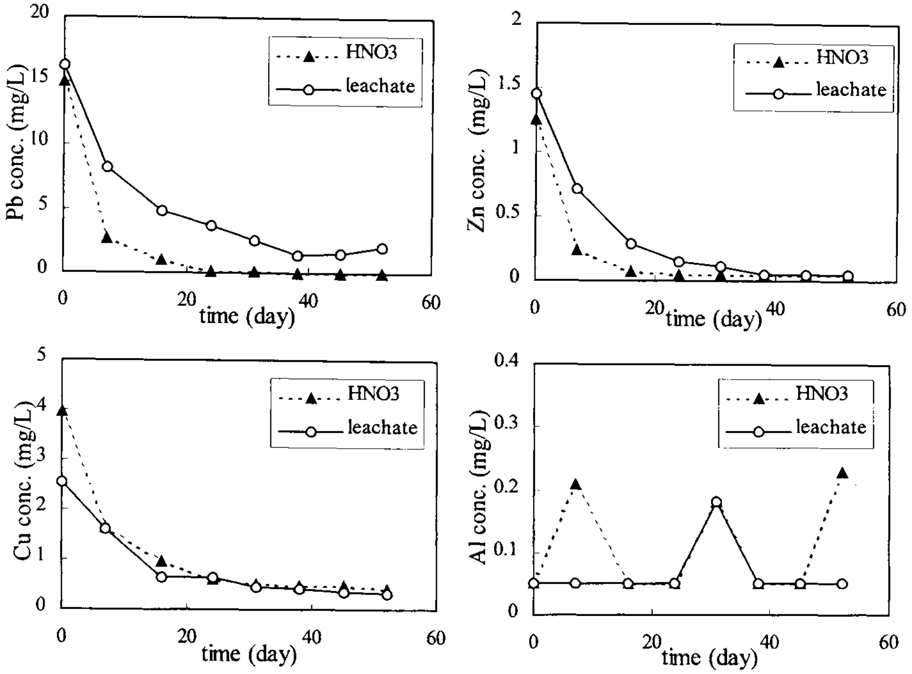


Fig. 5 Time course of metal leaching concentration in the leachate

The leachant is inbibed by the residues. After second leaching, 80-90% of the influx is leached out as the leachate. The pH of the leachate from both columns were almost same level; pH 12.2-12.6. Highly alkaline pH is kept for 56 days, even though the acid is a leachant.

Leaching concentration of Pb, Zn, Cu and Al in the leachate are shown in Fig. 5. Cd was not detected in any leachate due to high pH. Pb, Zn and Cu leached out in the highest concentration during the first leaching step, and then decreased with time. The leachate from column B (the leachant is JLT-13 leachate) always showed higher concentration of Pb and Zn than that of column A (HNO_3 leachant), because the leachant contains Pb (23.6 mg/L), Zn (7.48 mg/L) originally. However, the concentration in the leachate is lower than the original leachant; Pb is 5-46% and Zn is 0.5-13%, respectively. This suggests that Pb and Zn adsorbed onto the residues. Indeed, there are numerous reports that MSWI residues have an adsorptive ability for metals [3-6]. The difference between Pb and Zn is caused by the mobility of metals. Cu leaching behaviour was different from that of Pb and Zn at two points. The highest leaching can be seen in the first leaching step similarly. However, the leaching concentration in the acid leachant was higher than that in the alkaline leachant. In the first step and the second steps, the efflux quantity of Cu was higher than the influx quantity; the leaching ratio of the first step was 330% and that of the second step was 210%. After the third step of leaching, the leaching ratio was 41-80% of the influx. Cu also adsorbed onto the residues, but the leaching at early stages (it is called as "initial wash-off") was larger than the adsorptive effects. Furthermore, acid is more effective in leaching of Cu than Pb and Zn. No obvious trend in Al leaching was observed. The reason is not clear.

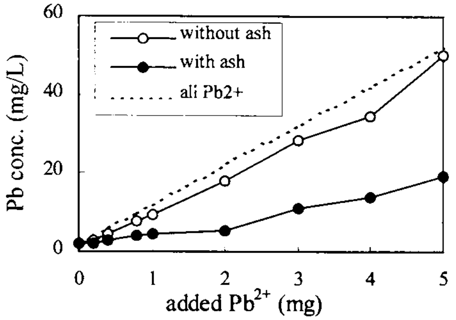
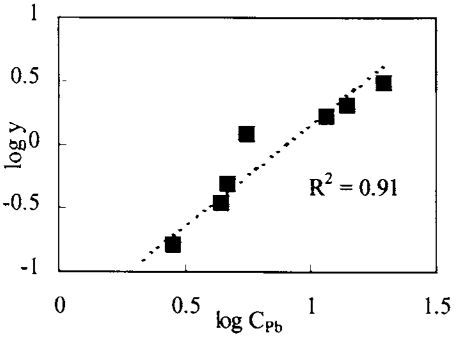


Fig.6 Pb concentraton in the solution with ash and without ash. (left: Fly ash A, right: Fly ash B)

Pb adsorption onto the residues was confirmed in the next experiment (Fig. 6). Open circles show dissolved Pb concentration in the leachate without ash and solid circles show dissolved Pb concentration in the leachate with ash. The lines do not start at the origin, due to the leaching of Pb from ash. The dissolved Pb concentration with ash is significantly lower than the concentration without ash, although the final pH of the leachate with/without fly ash is almost same values; 12.3-12.4 for fly ash A and 12.9 for fly ash B. These phenomenon are discussed based on Freundlich's adsorption isotherm ,which is one of the most typical adsorption isotherm. Logarithm of Pb concentration (log C_{Pb}) were plotted to X-axis and logarithm of y, the quantity of adsorbate per unit of weight of adsorbent, were plotted to Y-axis (Fig. 7). A positive correlation ($R^2 = 0.91$) can be seen and Pb adsorption onto fly ash A is confirmed.

The adsorptive quantity based on the differences of dissolved Pb concentration are calculated. When L/S = 100 and the dissolved Pb concentration is 50 mg/L (52.0 mg/L for fly ash A and 56.1 mg/L for fly ash B), the adsorbed quantity is 3.11 mg/g for fly ash A and 1.65 mg/g for fly ash B respectively. The quantity of Pb adsorbed on the residues are different for



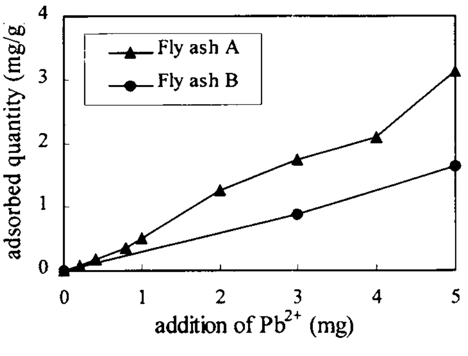


Fig. 7 Fleundlich's isotherm of Fly ash A

Fig. 8 Pb adsorbed quantity vs. added quantity

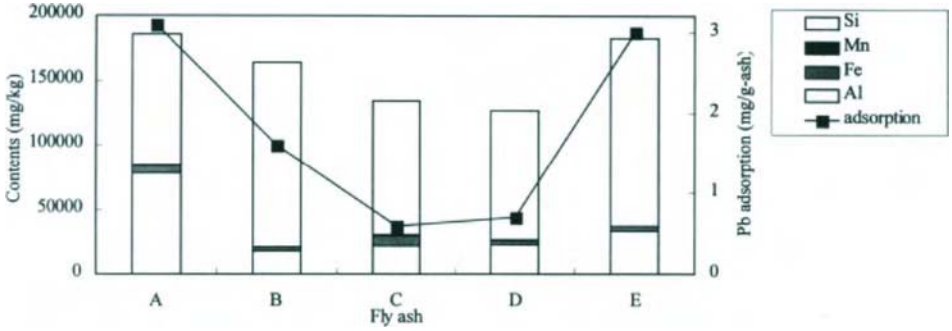


Fig. 9 Relationship between element contents and Pb adsorption quantity

both fly ash, due to the difference in the residue composition. 5 kinds of fly ash from stoker type of MSWI were used as samples and performed the same batch experiments for sorption behaviour in order to study the relationship between composition and adsorptive ability in the 50 mg/L of Pb concentration. The pH of the solution are: pH 12.4 (fly ash A), pH 13.0 (fly ash B), pH 13.0 (fly ash C), pH 13.0 (fly ash D), pH 12.7 (fly ash E). As Pb adsorption rate onto coal fly ash is reported at pH higher than 9, we judged residues that the adsorption ability could be compared. We focused on the contents of Fe, Mn, Al, Si, Ca as the possible adsorbents as heavy metls can adsorb onto iron oxide, calcite ($CaCO_3$), ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_20$), and alminosilicates [5-10]. There was a positive correlation between total contents of "Fe + Si + Mn + Al" and adsorptive ability for these 5 types of fly ash (Fig. 9).

4. CONCLUSIONS

The conclusions described from this study are shown as below:

1. Small-scale column experiments simulating a monofill landfill site were performed. The leachate of JLT-13 of MSWI fly ash and HNO_3 (pH 4) were used as a leachant. The quantity and the pH of the leachate from both columns were almost identical, regardless of the different of initial pH.
2. When we poured the leachate of MSWI fly ash, Pb and Zn concentration decreased. It was suggested that Pb and Zn is adsorbed onto MSWI residues.
3. The experiments adding dissolved Pb with/without ash showed adsorption phenomenon onto the ash. The adsorption behaviour was of the Fleundlich type.
4. The adsorptive quantity of Pb was 3.11 mg/g-ash for fly ash A and 1.65mg/g-ash for fly ash B, when the L/S = 100 and Pb concentration is 50 mg/L. The difference is due to the composition of the residue. There was a positive correlation between total contents of "Fe + Si + Mn + Al" and adsorptive quantity of MSWI residues.

5. REQUIREMENTS

1. Quantification of the maximum quantity of Pb adsorption onto MSWI residues are

2. Qualification of the adsorptive ability when pH is changed is required.
3. Study and discussion of adsorptive behaviour and the acid neutralizing capacity of the material are necessary, as the adsorptive ability of Pb onto the MSWI residues in neutral area and alkaline area are stronger than that of acidic area.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Assessment of the leaching due to degradation factors of stabilised/solidified waste materials

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In the Netherlands, only a few applications of Stabilised/Solidified waste materials (S/S-waste materials) are known due to an uncertain long term behaviour of the S/S-waste material. This paper presents an assessment tool to determine the leaching due to degradation factors of S/S-waste materials. The tool is carried out on two cases: stabilised/solidified industrial purification sludge with cement, indicated with A and melted/crystallised sewage sludge. By means of a life time prediction procedure of CIB/RILEM relevant durability tests for the two cases are selected: wet/dry, erosion and freeze/thaw. If assuming that leaching of hazardous components can be calculated by multiplication of available components with material loss after the durability test and by means of normalisation with Dutch leaching standards, it is clear that erosion of stabilised/solidified industrial purification sludge with cement has the highest contribution to the leaching, even if it is acknowledged that the material loss after erosion is overestimated by 100%. The contribution of the tool to the decision making process can be more transparency of leaching due to degradation factors, thereby helping the decision makers to chose between different S/S-treatments and to chose the best application of the S/S-waste material.

1. INTRODUCTION

In the Netherlands, only a few applications of stabilised/solidified waste materials are known due to an uncertain long term behaviour of the S/S-waste material, an expected negative image of the product and complex legislative procedures [2]. In some cases it is obvious that more information about the impact of external influences on the leaching characteristics of S/S-waste materials is needed.

Stabilisation/solidification of hazardous waste materials aims at reducing the emission of hazardous components. Even if the material is exposed to serious degradation factors, emissions have to be minimal. Some S/S-waste materials are expected to be more resistant to these factors than others, while these materials are often more expensive than others. Though in recent research S/S-waste materials are exposed to durability tests, change in emission due to these tests is hardly examined.

This paper presents an assessment tool to determine the differences in emission of inorganic components between two types of S/S-waste materials after exposure of these materials to the main degradation factors. Aim of the assessment tool is to compare the leaching of certain S/S-waste materials with each other. The tool is based on the concept of durability. Durability is defined as the resistance of materials towards external influences. In the case of S/S-waste materials the definition may be restricted to minimising the leaching of hazardous components of S/S-waste materials exposed to external influences.

Content of this paper is the assessment of stabilised/solidified industrial purification sludge with cement and melted/crystallised sewage sludge with the presented tool in order to evaluate the tool. A sensitivity analysis is carried out to detect uncertainties in degradation of the S/S-waste materials.

Firstly, two S/S-waste materials are selected. Secondly, a life time prediction procedure is used to select relevant durability tests. Afterwards, the experimental method is described and the experimental data of durability tests on the two S/S-waste materials are given. The assessment is carried out for the two cases. A sensitivity analysis shows the relative importance of the conclusions from the assessment. In the end, conclusions are drawn and recommendations are given on the suitability of the tool in the decision making process.

2. SELECTION OF S/S-WASTE MATERIALS

For the sake of representative results, the most promising S/S-waste materials are selected. The minimum standard is that they fulfil the Dutch legislation concerning building materials. If possible, these S/S-waste materials are selected that have been used in practice. The purpose of these criteria is the selection of realistic S/S-waste materials, representing a relative high resistance to external influences. A disadvantage of the selection of S/S-waste materials used in practice is that each product is made of different amounts and types of hazardous waste materials. This disadvantage can be coped with by calculation of a degree of stabilisation/solidification.

The most promising technique in the Netherlands is stabilisation/solidification of a wide range of hazardous waste materials with inorganic binders, especially cement. There are only few applications known of this material. In this research stabilised/solidified industrial purification sludge with cement is examined, indicated with A. The second most promising and tested technique is melting/crystallisation of sewage sludge. Till now, this material is not used in practice. The material is indicated with B.

3. LIFE TIME PREDICTION PROCEDURE

Before the leaching due to degradation factors can be measured, these durability factors must be clear. By means of a life time prediction procedure of CIB/RILEM, relevant durability tests for the two cases are selected. This life time prediction procedure contains the following steps to be considered in this paragraph: problem definition and preparation.

The problem we stand for is the leaching due to degradation factors. The problem is defined by the following argument. Changes in leaching behaviour due to durability factors can be caused by chemical changes (like carbonation), physical changes (loss of material and surface extension) and mechanical changes (disintegration) of the material. Changes is leaching due to chemical, physical and mechanical changes are detected by material loss after a durability test and leaching before and after a durability test. The materials are exposed to the most extreme conditions, namely, no isolation to the ground(water) and no isolation from (wind)erosion and rainwater. In this extreme situation, changes in leaching are provided. Finally, the problem definition in our two cases is: changes in leaching of hazardous components of the stabilised/solidified industrial purification sludge with cement or melted/crystallised sewage sludge during the use of that material in a civil construction with no isolation to the ground(water) and no isolation from (wind)erosion and rainwater.

The second part of the life time prediction procedure is the preparation. The main degradation factors have to be identified. From the fact that the S/S-waste materials are not isolated from ground(water), (wind)erosion and rainwater and considering the two S/S-waste materials, the main degradation mechanisms are: freeze/thaw, erosion and wet/dry (solely for the cement bound waste material) [1]. Both materials are expected to lose material during freeze/thaw conditions and erosion. Contrary to the melted/crystallised waste material, the waste material bound with cement is sensitive to wet/dry conditions.

4. EXPERIMENTAL METHOD

The experiments, described in this paper, are meant to give insight into the leaching of the two selected S/S-waste materials. As will be made clear in this chapter, leaching due to degradation factors is simulated by durability tests. In preliminary investigations suitable durability tests were selected for S/S-waste materials [1]. The two selected S/S-waste materials are exposed to the durability tests given in table 1.

Table 1
Durability test per S/S-waste material

	A (stabilised/solidified industrial purification sludge with cement)	B (melted/crystallised sewage sludge)
Wet/dry (a modification of ASTM D559-96)	Yes	No
Erosion (NEN 2875)	Yes	Yes
Freeze/thaw (RILEM 4 CDC 3)	Yes	Yes

The specimens are exposed to the diffusion test NEN 7345 [5] before and after the durability test. Besides that, after each of these durability tests, the loss of material is detected. Because of the need to know the leaching of hazardous components, the material loss is multiplied with the availability of hazardous components. Therefor on both specimen A and B the availability test NEN 7341 is carried out [4]. The equation used is:

$$L_{rn} = (\Delta m_n \times A_r) + \Delta L_{rn} \qquad (1)$$

L_{rn} = leaching of component r due to durability test n (mg/m^2)
Δm_n = material loss durability test n(kg/m^2)
A_r = availability component r (mg/kg)
ΔL_{rn} = change in leaching of component r detected with diffusion test (kg/m^2)

Experiments showed that for these S/S-waste materials no significant changes in diffusion due to durability tests occurred. Therefor, the factor ΔL_{rn} is left out.

5. EXPERIMENTAL DATA

The following tables show the availability of the two S/S-waste materials and the material loss after wet/dry, erosion and freeze/thaw. Three components (barium, copper and zinc) were analysed, because of the presence of these components in the S/S-waste material and because of the existence of leaching standards for these components.

Table 2:
Availability of barium, copper and zinc

	A (mg/kg)	B (mg/kg)
Barium	113,8	58,4
Copper	23,3	30,3
Zinc	220,2	117,1

Table 3:
Material loss after wet/dry, erosion and freeze/thaw

	A (kg/m^2)	B (kg/m^2)
Wet/dry	-0,020	-
Erosion	4,66	0,0917
Freeze/thaw	0,183	0,822

Figure 1 shows the leaching per durability test, obtained from the data above and equation (1).

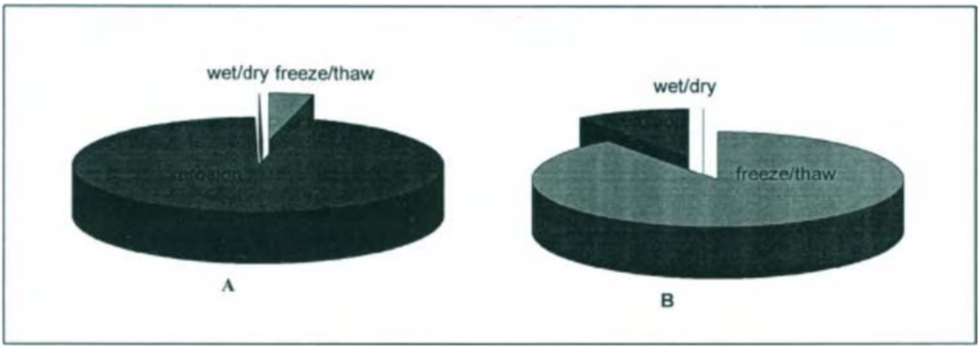


Figure 1. leaching per durability test of S/S-waste material A and B.

6. ASSESSMENT

Now that the data are clear the final question arises: what is the difference in emission of inorganic components between the two types of S/S-waste materials after exposure of these materials to the main degradation factors. An answer is not directly obvious from the data. The following reasoning is followed in the development of an assessment tool:

1. The two types of S/S-waste materials can be compared with each other by means of normalisation with Dutch leaching standards for building materials. The ratio of the detected leaching of components to the Dutch leaching standards for building materials is defined as the degree of stabilisation/solidification [6].
2. Overall leaching of all hazardous components can be calculated by adding up L_r for each r;
3. Overall leaching for all durability tests can be calculated by adding up the leaching due to the durability tests;
4. Weighted summation is a suitable standardisation method for this problem [3].

These arguments lead to an assessment tool for the leaching due to degradation factors of S/S-waste materials. The equations are:

$$D_m = L_m / I_r \qquad (2)$$

$D =$ Degree of stabilisation/solidification
$I_r =$ standard component r from legislation concerning building materials (mg/m^2)

$$L = 1/N \sum_{n=1}^{N} \{ \ 1/R(\sum_{r=1}^{R} D_m) \qquad (3)$$

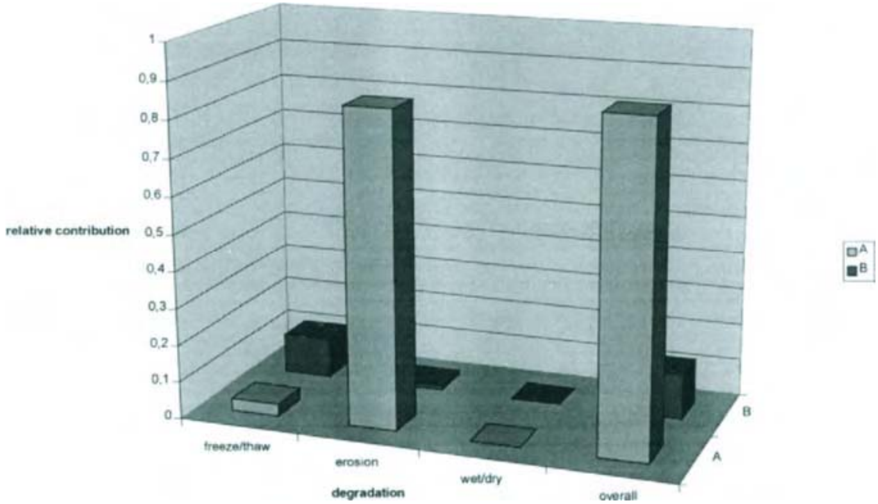
L = overall leaching due to degradation factors (-)
N = amount of durability tests (-)
R = amount of components (-)

In legislation concerning building materials use of secondary and primary building materials is limited by emission standards. These standards prescribe the highest allowed transport of components into the soil due to leaching of the building material. Relevant standards from legislation concerning building materials are given in table 4.

Table 4
Standard component r from legislation concerning building materials

	Standard (mg/m^2)
Barium	6300
Copper	540
Zinc	2100

Interpretation of data obtained from durability and availability tests, will give insight into the leaching due to degradation factors. The figure below shows the leaching of the two S/S-waste materials per durability tests and overall leaching due to degradation factors.



the data change? To answer this question a sensitivity analysis is carried out. Looking at the leaching of A, see figure 2, it is clear that erosion has the highest contribution to the leaching due to degradation factors. Moreover, erosion of A makes the difference between materials A and B. The sensitivity analysis is limited to erosion, because changes in leaching after erosion has the highest impact on the assessment of A and B.

Leaching after erosion is a multiplication of availability and material loss per component, see equation (1). The high score on leaching is due to the high material loss after the erosion test. Suppose, the data obtained from the erosion-tests are not valid and suppose the data are overestimated by 100%, then the real material loss is the half of the data obtained from the erosion-test. Figure 3 shows the assessment with this reduction of material loss after erosion.

7. CONCLUSIONS AND RECOMMENDATIONS

In this final chapter answer to the question of the suitability of the tool in the decision making process will be given. Therefor, firstly the experimental data of wet/dry, erosion and freeze/thaw tests on stabilised/solidified industrial purification sludge with cement and melted/crystallised sewage sludge are discussed.

If assuming that leaching of hazardous components can be calculated by a degree of stabilisation/solidification and by adding up available components and the leaching due to different durability tests, the following data are clear. Erosion of material A (stabilised/solidified industrial purification sludge with cement) has the highest contribution

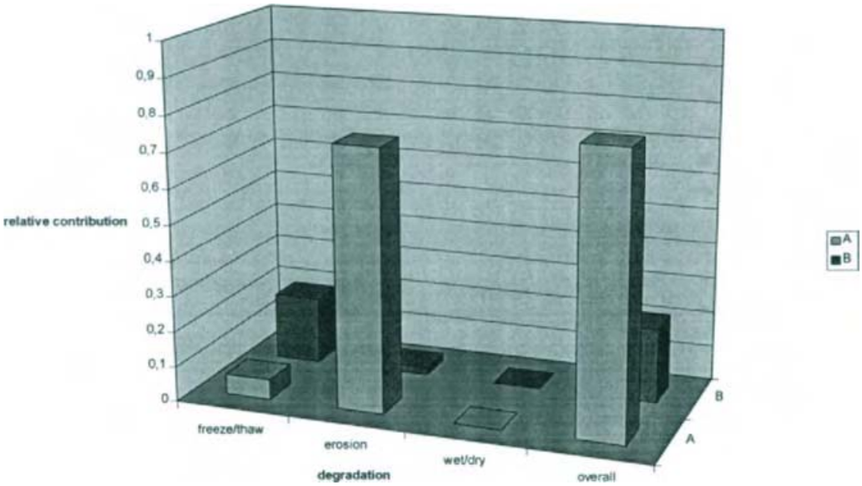


Figure 3. sensitivity analysis: reduction of material loss of A after erosion with 100%.

to the leaching, even if it is acknowledged that the material loss after erosion is overestimated by 100%. Because of degradation during erosion, A presents the highest leaching due to erosion. B (melted/crystallised sewage sludge) is most sensitive to material loss during the freeze/thaw-test. Leaching after freeze/thaw of material B is higher than of material A, detected with the method described in this paper.

The assessment tool is meant to contribute to an effective decision making process. At present there is often uncertainty about the leaching of hazardous components. The presented assessment tool can give insight into the leaching due to material loss after degradation factors. The data obtained with the tool have still to be interpreted by the decision maker. For example, they need to be aware of the autonomous leaching not caused by degradation factors. In addition, decision makers have to decide for themselves the relative weight of leaching to for instance financial costs. The contribution of the tool can be more transparency of leaching, thereby helping the decision makers to chose between different S/S-treatments and to choose the best application of the S/S-waste material.

Besides these contributions of the tool to the decision making process, more information about the suitability of the used durability tests and more data of leaching of S/S-waste materials is needed. Due to partly unknown suitability of durability tests, the relation of the durability tests to degradation in practice have to be made clear. If the need for more data is fulfilled, the assessment tool can be less time consuming. For instance, if more assessments are carried out, they may show that one or two degradation factors have highest contribution to the leaching. Therefor, the amount of prescribed durability tests can be reduced.

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Reuse of secondary lead smelter slag in the manufacture of concrete blocks

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A secondary lead smelter slag has been used in a cement based stabilization/solidification process for the manufacture of concrete blocks. The influence of the lead slag on the hydration chemistry has been studied by means of cementitious mixtures containing up to 65% powdered slag. The results have shown that the hydration chemistry is not negatively influenced from both the qualitative and quantitative points of view, provided that the lead slag content is within 30%. Concrete blocks containing 15% cement have been produced by partial substitution of the whole aggregate and each differently sized aggregate class. The maximum amount of substitution was 22%. Blocks of unconfined compressive strength ranging between 23.0 and 25.6 MPa can be produced in this way. The feasibility of the stabilization process has been tested by means of two dynamic leaching tests making use of a CO_2-saturated solution and distilled water. The duration of the tests was extended up to 32 days to get information on the long term behaviour of the stabilized products. In this regard, it has been found that lead is released in cumulative amounts of the order of a few parts per million and that the resistance to lead diffusion is high.

1. INTRODUCTION

The most recent directives of European Community regarding solid wastes management give high priority to the development of technologies addressed towards recycling and reuse. In the former case, wastes are recycled to the same process from which they were generated, while in the latter they are reused in a different process. High priority is also given to the recovery of raw materials and energy from wastes. These requirements cannot be always satisfied because a proper technology may be too expensive or may not be available at all. When this happens, the last chance is given by treatment processes addressed to the reduction of the environmental impact of wastes. In the case of solid wastes, stabilization/solidification (S/S) processes are the most suitable [1].

S/S processes are already widely used for the treatment of hazardous industrial solid wastes, and those cement-based are most suited for wastes containing heavy metals [2]. Although they are mainly employed for wastes safer disposal, they are also intrinsically able to give products which may have a high potentiality to be used in the field of pre-formed building materials. This is due to the fact that these processes often lead to the formation of monolithic products.

In any case of a specific waste stabilized by means of a specific binding matrix, a fundamental study is required to assess the actual potentiality of the S/S process to be addressed towards the manufacture of building materials instead of safer disposal. First of all, the output of this type of fundamental study must be the understanding of the chemical interactions that occur between the hydrating binder and the waste components (pollutants). This is particularly important when severe negative effects are known to take place in the presence of specific contaminants, and this is just the case of the waste used in this work.

The waste is a secondary lead smelter slag that comes from exhausted automotive batteries processing for the recovery of metallic lead. It is a hazardous waste classified in the European Waste Catalog with the code 10.04.01 and is produced in Italy at the rate of 10,000 ton/year. This slag contains lead in amounts ranging typically between 10 and 20% and this can be of concern as it is well known that this metal has a strong negative effect on the hydration processes that are responsible for setting and hardening of cements [3-7]. Therefore, it appears most important to undertake a fundamental chemical investigation to assess the real possibilities of reusing the slag with a relatively high lead content for the manufacture of concrete blocks as well as the limits of this application.

In addition to this, it must be checked that the proposed process is environmentally acceptable through leaching tests properly designed to understand the long-term behaviour of the products in the presence of two different leaching media, namely CO_2-saturated solution and distilled water. A test that makes use of a CO_2-saturated solution is currently employed in Italy for the characterization of hazardous wastes, while a test that makes use of distilled water is at the moment under development and will replace the former in the near future. It is useful to point out that these tests have the specific purpose of waste classification, and their total leaching time is 48 hours at most. This time was extended up to 32 days to get information on the long-term behaviour of the products of waste stabilization.

Finally, a preliminary physico-structural characterization must be carried out through the determination of the unconfined compressive strength. This is the most important property whose knowledge is necessary to foresee a possible technological application.

2. EXPERIMENTAL

The lead slag has been characterized by means of chemical analysis to get the composition in terms of main components concentrations, as follows: Al_2O_3 2.17%, Fe_2O_3 68.20%, PbO 13.79%, SiO_2 6.28%, CaO 4.09% and CuO 1.83%. The bulk density has been found to range between 2,500 and 3,000 kg/m^3 for samples of particle size < 10 mm and between 10 and 20 mm, respectively. The two size fractions are approximately 50% each of the whole material.

Hydratory mixtures of pozzolanic cement (CEM IV/A 32.5R) with 0, 15, 30 and 65% lead slag were prepared and cured at 25°C and 100% R.H. for times ranging from 2 hours to 14 days. The slag used in the above mixtures was ground to pass a 0.5 mm sieve.

At any pre-fixed curing time, hydration was stopped by grinding the samples under acetone with subsequent rinsing with diethyl ether and final drying. Stopped samples were stored in a desiccator for later analysis.

Simultaneous thermogravimetric (TGA) and differential thermal (DTA) analyses were carried out to get data on the amount of water chemically combined and nature of neo-formed hydration products.

The slag was also used for partial substitution of the aggregate in the manufacture of concrete blocks. In the manufacture of concrete blocks, the ideal aggregate size distribution (Füller grading curve) is matched by properly mixing three different granular materials classified as fine aggregate, medium aggregate and coarse aggregate. In our case, the slag has been used for the partial replacement of the whole aggregate as well as of each individual aggregate class (fine, medium and coarse) to get a total of four different systems, referred to as systems W, F, M and C, respectively. This allows the effect of slag specific surface to be studied. In system W, in which the slag partially replaced the whole aggregate, the slag as received was used. In systems F, M and C, those in which the slag partially replaced each aggregate class at a time, the slag was sieved and ground to get the proper size distribution. Figure 1 shows the size distribution of the slag as received and the three aggregate classes used.

Concrete composition for all the four types of blocks is reported in Table 1. It should be noted that the aggregate and slag sum 85% in any case. On this basis, the amount of aggregate substitution is 22% for the system W and 12% for the systems F, M and C. It is also emphasized that concrete blocks composed of 15% cement and 85% ordinary aggregate give mechanical performance such that they belong to class C20/25. This means that at least 95% of unconfined compressive strength determinations must be greater than 20 MPa for cylindrical samples of size DxH=10x15 cm^2, or greater than 25 MPa for cubic samples of size L^3=15 cm^3. According to Italian classification, 9 classes of concrete blocks exist ranging from C12/15 to C50/60 [8].

For each system, two series of cubic blocks were prepared and cured 28 days at 25°C and 100% R.H. These two series were of size 15x15x15 cm^3 for unconfined compressive strength determination, and of size 10x10x10 cm^3 for leaching tests.

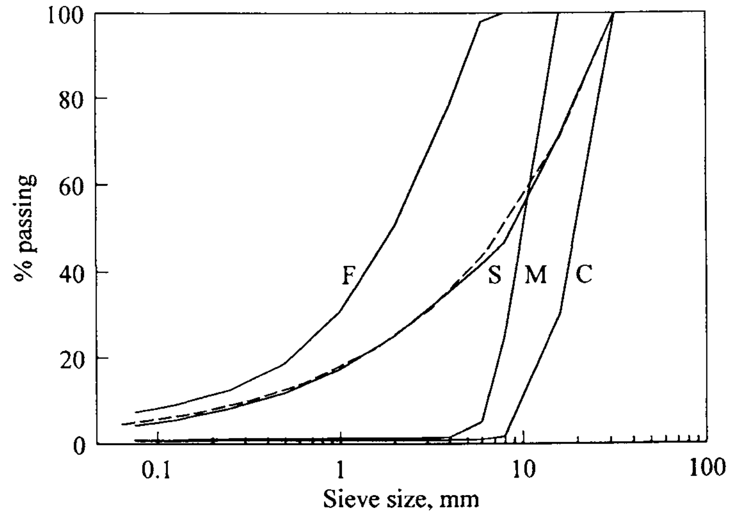

Figure 1 - Particle size distribution of slag as received (S) and aggregate fine (F), medium (M) and coarse (C) fractions. Dashed line is the Füller grading curve

Table 1 - Composition of the systems tested, wt%

System	Binder	Aggregate	Lead slag
W	15	66	19
F, M, C	15	75	10

Both leaching tests are dynamic. They make use of distilled water and CO_2-saturated solution. In the latter case, CO_2 was continuously fed to the leaching vessel to keep the solution constantly saturated. In both tests the liquid to solid ratio was 5:1 (vol/vol) and the renewal times were 2, 8, 24, 48, 72, 102, 168, 384 and 768 hours (32 days).

3. RESULTS AND DISCUSSION

Figure 2 shows typical results of thermal analysis in terms of TGA and DTA curves for the samples containing 30% slag cured 2 hours, 8 hours and 14 days.

The DTA traces show endotherms related to dehydration of reactants and products, as follows [9,10]. Those at 53°C (2 h), 69°C (8 h) and 97°C (14 d) are due to calcium silicate hydrate, those at 88°C (2 h), 111°C (8 h) and 121°C (14 d) are due to calcium trisulphoaluminate hydrate (ettringite), those at 139°C (2 h) and 143°C (8 h) are due to gypsum and finally those at 176°C and 458°C (14 d) are due to calcium monosulphoaluminate hydrate and calcium hydroxide, respectively.

Gypsum is a reactant added to raw cement as set retarder. The endotherm related to its presence decreases in intensity from 2 to 8 hours and is completely absent at 14 days. Ettringite is the hydration product kinetically favoured and the intensity of the related endotherm constantly increases with curing time. Calcium silicate hydrate and calcium hydroxide are the main cement hydration products. The former is present as early as after 8 hours, while the latter is present only at 14 days. Calcium monosulphoaluminate hydrate is formed from ettringite when gypsum is a limiting reactant [11].

From the qualitative point of view, the behaviour of the system of Figure 2 (30% slag) is the same as that of pure binder (thermograms not shown), and this makes clear that the presence of lead slag in the mixes up to 30% does not alter significantly the binder hydration chemistry.

The amount of water chemically combined has been determined by recording the mass loss from room temperature to 500°C (TGA traces). This temperature is higher than the dehydration temperature of all the hydration products, and lower than the onset of lead oxidation reaction, which is clearly seen to occur in the sample cured 2 hours from the mass increase at temperature higher than 510°C.

The TGA traces show that the mass increase at high temperature is very low for the sample cured 8 hours and completely absent for the one cured 14 days. This is a result of outstanding importance because it proves that lead is microencapsulated within the stabilized product in such a way that its oxidation is completely inhibited when the hydration degree is high. Evidence of the occurrence of a chemical mechanism responsible for lead stabilization was found in a previous work [12]. According to Bhatt [13], this mechanism relies on the formation of a complex metal silicate hydrate.

The quantitative results of chemically combined water determined as previously described are summarized in Table 2 for the pure binder and the mixes containing 30 and 65% slag. In the cases of binder-slag mixes, the values of mass loss directly read from the thermograms have been normalized in respect to the amount of binder present.

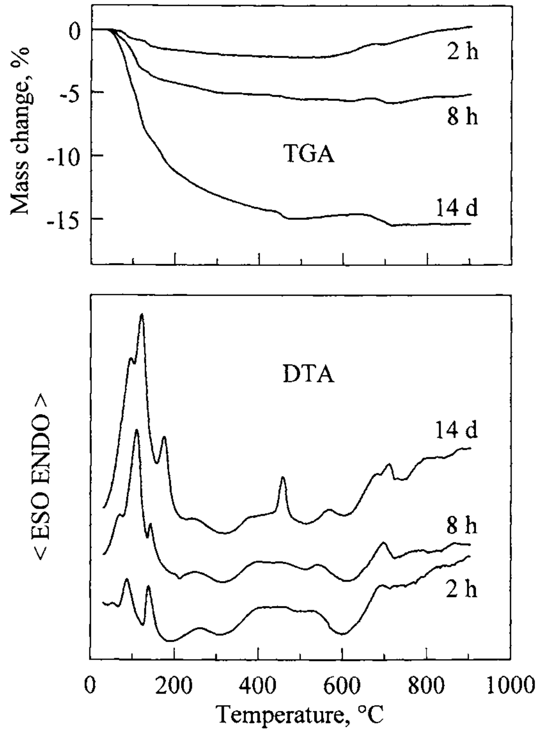

Figure 2 – Results of thermal analysis carried out on samples containing 30% slag

The chemically combined water data show that hydration is not negatively affected by the slag up to 30% also from the quantitative point of view.

The quantitative results are of great importance because the slag was ground to a < 0.5 mm size to increase the specific surface and enhance the chemical effects due to lead solubilization in the strongly alkaline pore solution of hydrating cement.

Table 3 shows the results of unconfined compressive strength determination on the samples of size 15x15x15 cm^3. Although no hardening was observed for system F, the one in which the slag has the highest specific surface area, the values measured in the other cases are remarkably good. To this regard, it should be kept in mind that each value of strength reported in Table 3 is the arithmetic mean of eight determinations for any of the compositions tested. Then, they have scarce statistical significance in relation to the classification of blocks, which, as previously stated, requires that at least 95% determinations must be greater than fixed thresholds. Despite this, it can be said that it is highly probable that blocks of composition C belong to the class C20/25 and blocks of compositions W and M could reach compressive strength values high enough to belong to the same class simply by means of optimization of aggregate substitution and/or use of additives such as soluble silicates. The latter chance can be worthy of consideration inasmuch as soluble silicates can precipitate heavy metals such as lead. As pointed out before, this metal undergoes partial solubilization in the strongly alkaline pore solution of hydrating cement and this is the reason why it has negative effects on cement hydration. Obviously, lead solubilization is a surface-dependent process and can take place to high extent in system F, where the aggregate fine fraction is partially replaced by the slag. Therefore, when the slag specific surface is high, hardening is inhibited.

Last but not least, it is very important to point out that our systems contain 15% cement and this is the binder content required for the manufacture of class C20/25 ordinary concrete blocks. Hence, the results obtained in this work nearly match the performance that can be given by blocks manufactured with traditional aggregate.

The results of the leaching tests are summarized in Figures 3 and 4 and Table 4. Figure 3 shows the cumulative amount of lead released in the CO_2-saturated solution leaching test. The ultimate values are of the order of a few parts per million. Lead release steeply increases up to about 168 hours; then the slope greatly decreases showing a strong effect of the monolithic matrix on lead diffusion outwards from the samples. In this case the leaching solution is quite aggressive, being kept constantly saturated by a continuous CO_2 feed. Hence, pH (see Table 4) does not change very much and small variations only occur during the initial steps of leaching. Therefore, it is believed that in these conditions the physico-structural characteristics of the monolithic samples limit lead release, while chemical factors are of lesser importance.

The values of unconfined compressive strength suggest that the physico-structural characteristics of systems W and M are similar, while those of system C are better than those of the other two. Therefore, even from the point of view of lead release, it may well be that systems W and M behave similarly, despite the much higher content of lead slag (with a finer particle size distribution) present in system W, while system C behaves better. This consideration is supported by the lower slope of the final portion of the curve for system C in respect to systems W and M. Therefore, system C shows a greater resistance to lead diffusion.

Table 2 - Normalized chemically combined water, wt%

Curing time	System		
	Pure binder	30% slag mix	65% slag mix
2 hours	4.1	3.1	7.1
8 hours	8.1	7.8	6.3
14 days	19.3	21.3	6.9

Table 3 - Unconfined compressive strength for concrete blocks, MPa

System	Strength
W	23.0
F	No hardening after 28 day curing
M	23.9
C	25.6

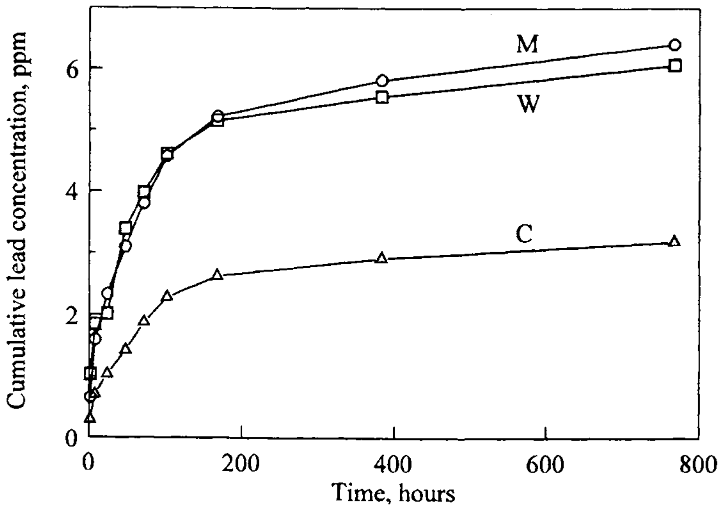

Figure 3 - Results of CO_2-saturated solution leaching test

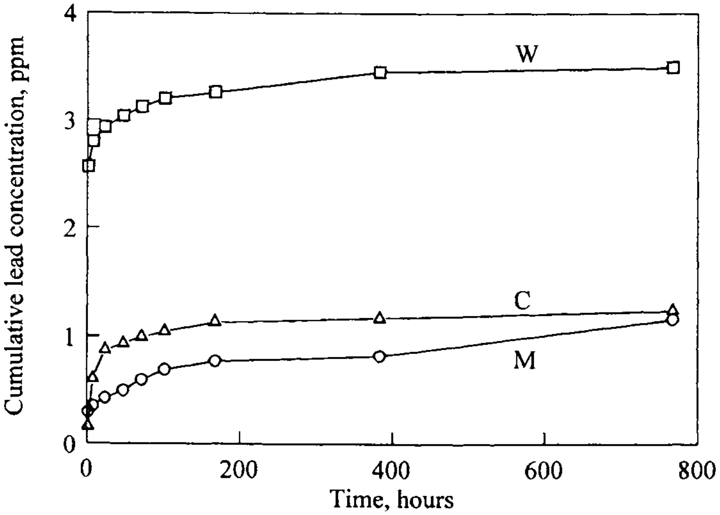

Figure 4 - Results of distilled water leaching test

Table 4 - pH values at the end of each leaching medium renewal

System	Renewal time, hours								
CO_2-saturated solution leaching test									
	2	8	24	48	72	102	168	384	768
W	4.4	5.0	4.9	5.0	4.9	4.9	5.4	4.9	5.4
M	4.7	5.8	5.4	5.4	5.8	5.5	5.0	5.0	5.0
C	4.9	4.9	5.3	5.3	5.5	5.6	5.3	5.5	5.6
Distilled water leaching test									
	2	8	24	48	72	102	168	384	768
W	5.8	5.9	6.3	6.4	6.6	7.0	7.4	10.5	10.5
M	5.4	5.4	6.0	6.0	6.1	6.2	8.7	10.8	10.8
C	4.8	5.4	5.9	7.0	7.5	9.3	10.0	10.0	10.0

Figure 4 shows the cumulative concentration of lead released in the distilled water leaching test. Even in this case the amount released reaches only a few parts per million. For all the systems tested, lead is rapidly released with a "wash-off" mechanism and the ultimate cumulative concentration as well as the slope of the final curve portion are both lower than those observed in the CO_2-saturated solution test. The initial rapid release depends on the amount of lead present in the system, while the final slow release depends on the leachant quality that is scarcely aggressive. This consideration is supported by the pH values measured in this case. They are strongly influenced by the matrix characteristics and are almost constant between 10 and 11 in the last two renewals.

Some final comments on the leaching tests are necessary, as they are not compliance tests. As stated before, their main purpose was the understanding of the long term behaviour of the stabilized products. From this point of view, both tests have shown that the release is initially rapid and then slows down indicating that the stabilized products offer a high resistance to lead diffusion. These results support the authors' opinion that the development of compliance tests for the utilization of stabilized products should mainly take into account the slope of the final portion of the release curve, instead of the extent to which the release occurs after times as short as 24-48 hours. The latter can be due to transient interactions between the stabilized products and the leachant, while the former characterizes the long term behaviour when the contact with the leachant may last indefinitely.

The leaching tests results reported in this paper should also be helpful for the development of the new Italian pertinent regulation that should have the scope to favour the utilization of the products of hazardous wastes S/S processes. In Italy, at the present time, stabilized products are characterized by means of the same tests as those for industrial solid wastes.

4. CONCLUSIONS

The work carried out on the secondary lead smelter slag allows the following conclusions to be drawn.

From both the qualitative and quantitative chemical points of view, the presence of powdered lead slag up to 30% does not negatively influence the binder hydration chemistry.

Concrete blocks of the Italian class C20/25 can be produced with partial aggregate substitution either directly or by simple manufacturing optimization.

The stabilization process based on pozzolanic cement has proved to be very effective. When submitted to the leaching tests with CO_2-saturated solution and distilled water, the stabilized products release cumulative amounts of lead of only a few parts per million. Also, the ultimate slope of the release curve is remarkably low, indicating a high resistance to lead diffusion.

Results of the type presented in this paper should be taken into account in the development of standards for the utilization of the products of S/S processes.

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Calcium sulphoaluminate cements made from fluidized bed combustion wastes

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Wastes generated in a bench-scale atmospheric fluidized bed combustor, using two different coals and a high-lime limestone sorbent, were employed as raw materials for the synthesis of calcium sulphoaluminate ($4\ CaO{\cdot}3\ Al_2O_3{\cdot}SO_3$) -based cements, which can be utilized for a wide range of applications. Raw mixes containing the bed material were heated in an electric oven in the temperature range 1000°–1200 °C. The best results in terms of reactants conversion and selectivity towards $4\ CaO{\cdot}3\ Al_2O_3{\cdot}SO_3$ were obtained at 1200 °C with the addition of an external source of alumina which was required to avoid melting phenomena or integrate the Al_2O_3 content necessary for the $4\ CaO{\cdot}3\ Al_2O_3{\cdot}SO_3$ formation.

1. INTRODUCTION

A wide range of industrial wastes and by-products containing reactive lime, sulphate and alumina can be usefully employed for the manufacture of calcium sulphoaluminate (CSA) cements. In the past the utilization of chemical gypsum, blast-furnace slag, bauxite fines and fly ash coming from pulverized coal-fired plants was investigated [1-12]. In this paper the use of fluidized bed combustion (FBC) ashes as raw materials for the synthesis of CSA cements is explored with the purpose of exploiting the Al_2O_3 content of coal ash as well as the CaO and $CaSO_4$ contents of exhausted SO_2 sorbent. First the characteristics of FBC ashes together with the properties and the uses of CSA cements are described. Then are presented and discussed the preliminary results of an experimental investigation on the synthesis of raw mixes containing wastes generated in a bench-scale atmospheric fluidized bed combustor.

2. CHARACTERISTICS OF FBC ASHES

Compared to traditional coal-fired plants, FBC technology [13-15] has many advantages such as: a) high mass and heat transfer coefficients; b) low combustion temperatures, around 850 °C; c) possibility of removing "in situ" sulphur dioxide from flue gases, using limestone-based sorbents as bed materials; d) good aptitude to the burning of low-rank coals and alternative solid fuels. On the other hand FBC reactors have some disadvantages like the considerable fines generation (elutriation) and the occurrence of severe erosion phenomena [15,14]. However the main problem is probably represented by the high quantity and low quality of generated wastes.

The desulphurization process at the operating conditions of 850 °C and 1 atm consists of two steps:

$$CaCO_3 \Rightarrow CaO + CO_2 \qquad (1)$$

$$CaO + SO_2 + \tfrac{1}{2}O_2 \Leftrightarrow CaSO_4 \qquad (2)$$

The limestone calcination according to reaction (1) is complete, while the sulphation (2) is an equilibrium reaction. Taking also into account that the CaO-SO_2 reaction mechanism does not allow a complete lime conversion [13], calcium/sulphur molar ratios largely exceeding the stoichiometric value (Ca/S=1) are typically employed in order to enhance the sulphur removal from flue gases. Hence in situ SO_2 removal requires sorbent amounts larger than those used in the common desulphurization processes [16].

As far as the quality of FBC ashes is concerned, their chemical composition is quite different from that of combustion wastes originated in the traditional plants. In fact FBC wastes contain considerable CaO and $CaSO_4$ amounts responsible for exothermal and expansive phenomena which make more difficult both disposal in landfill and re-use in cement and concrete industry [16]. Furthermore, the low FBC operating temperatures hinder the formation of a glassy state and markedly reduce the ash reactivity towards CaO, giving rise to a pozzolanic activity degree lower than that of fly ashes generated in the common coal-fired power plants. There is therefore an urgent need of finding new application fields for FBC wastes.

3. PROPERTIES AND USES OF CSA CEMENTS

The interest towards CSA cements is due to their peculiar properties. Their main component, calcium sulphoaluminate ($C_4A_3\bar{S}$[1]), can be synthesized at temperatures 200°–300°C lower than those required by the formation of ordinary Portland cements (OPC). Moreover, CSA cements need a lower amount of limestone in the raw mix and this leads to a reduction of both the thermal input for the calcination process and the emission of CO_2, gas mainly responsible for the greenhouse effect. Finally, the clinkers resulting after firing are relatively soft and require less grinding energy than OPC clinkers. Consequently these binders can give a substantial contribution to the saving of natural resources, energy and environment [1,7,8,9,10].

The technical behaviour of sulphoaluminate cements is mainly due to the formation of ettringite, $C_6A\bar{S}_3H_{32}$, by $C_4A_3\bar{S}$ hydration. Calcium sulphoaluminate can react with water in two ways: together with lime and calcium sulphate to give only ettringite (reaction 3); combined with calcium sulphate alone to give ettringite and aluminium hydroxide (reaction 4);

$$C_4A_3\bar{S} + 6C + 8C\bar{S} + 96H \Rightarrow 3C_6A\bar{S}_3H_{32} \qquad (3)$$

$$C_4A_3\bar{S} + 2C\bar{S} + 38H \Rightarrow C_6A\bar{S}_3H_{32} + 2AH_3 \qquad (4)$$

---

[1] according to the cement chemistry notation: C=CaO; A=Al_2O_3; $\bar{S}$=SO_3; S=SiO_2; F=Fe_2O_3; H=H_2O.

Ettringite synthesized in the reaction (3) has expansive properties which can be exploited by special binders like shrinkage-resistant and self-stressing cements [17,18]. On the other hand, ettringite generated in the reaction (4) is not expansive and has the important feature of giving high mechanical strength at early ages [12,3].

Other compounds such as C_2S, C_4AF, $C_5S_2\bar{S}$, C_2AS, CA, $C_{12}A_7$ and C_3A can occur in CSA cements depending on the composition and proportioning of the raw materials employed for their manufacture. Among these compounds only C_2S, which reacts with water to produce CSH like in OPC, is able to regulate strength and durability of the hydrated cements, especially at medium and longer ages. The other above mentioned phases have a poor hydraulic behaviour and provide a small contribution to the mechanical properties [19,20].

The commercially employed $C_4A_3\bar{S}$-based products are generally referred to uses in expansive binders for special applications. There are two kinds of these formulations: (1) cements having a high $C_4A_3\bar{S}$ content acting as additives for OPC; (2) modified OPC containing $C_4A_3\bar{S}$ instead of C_3A. In both cases $Ca(OH)_2$, derived from hydration of C_3S and C_2S present in OPC, produces the desired expansive effect, due to its combination with $C_4A_3\bar{S}$ and $C\bar{S}$.

Applications on industrial scale of CSA cements as structural and dimensionally stable materials have been made only in China. The first Chinese $C_4A_3\bar{S}$-based binders were manufactured more than 20 years ago and the present production is about 1 million tons per year. The main features of these cements are, besides a high early strength, good impermeability and freezing-resistance, low dry-shrinkage and solution alkalinity, outstanding chemical corrosion resistance [21]. In other countries the synthesis of rapid-hardening CSA cements has been already performed at laboratory scale or in pilot plants and there is an increasing interest, especially in Europe, towards them [22].

4. EXPERIMENTAL

The combustor wastes were generated in a stainless steel atmospheric bubbling fluidized bed combustor, 40 mm ID and 1 m high, electrically heated by means of two 2.2 kW ovens.

A Polish coal and a South African coal, both low (about 1%) in sulphur, were fed to the reactor. Their technical analysis is shown in Tab. 1. An Italian high-lime (96.8% $CaCO_3$) limestone was used as sorbent.

Table 1
Technical analysis of coals, % (dry basis)

	Polish coal	South African coal
Volatile matter	23.1	22.5
Ash	17.9	15.3
Fixed carbon	56.3	59.7
Moisture content	2.7	2.5

Table 2
FBC operating conditions

Bed temperature, [°C]	850
Air total flow rate, [nl/h]	500
Fluidization velocity, [m/s]	0.40
Coal-limestone mixture flow rate, [g/h]	60
Coal-limestone mixture size range, [μm]	425-600
Ca/S molar ratio in the mixture	3
Sand mass, [g]	150
Sand size range, [μm]	600-850

The operating conditions of the fluidized bed reactor are listed in Tab. 2.

The value of the air flow rate was chosen in order to ensure a complete coal combustion. The particles of the coal-limestone mixture, continuously fed to the reactor, had the same size range (425-600 μm) to allow an uniform mixing. A 600-850 μm silica sand, batchwise injected from the top of the combustor, was used as bed material. The sand size range, larger than that of the coal-limestone mixture, allowed to make easier its separation from the other bed residues (exhausted sorbent and coal ashes) by mechanical sieving.

In order to have higher freedom degrees in the proportioning of the raw mixes to be synthesized, FBC wastes were subdivided in two streams. The first was composed by elutriated ash (E) which was continuously collected by a cellulose filter at the top of the reactor; the second was constituted by the fraction of bed material (B), discharged from the bottom of the combustor at the end of the test, which passed the 600 μm–sieve.

FBC wastes-based raw mixes were synthesized in a laboratory electric oven for 2 hours at temperatures ranging from 1000° to 1200 °C.

X-ray fluorescence (XRF) and X-ray diffraction (XRD) analyses were used for the characterization of FBC residues. XRD analysis was also employed for recognizing both unconverted reactants and synthesized products within the fired mixes.

5. RESULTS AND DISCUSSION

5.1. Combustion of Polish coal

Chemical composition of E and B generated by the Polish coal combustion is shown in Tab. 3.

The main crystalline phases detected in both materials were quartz, lime and anhydrite.

Comparing the data listed in Tab. 3 it can be drawn that B and E were respectively enriched in exhausted sorbent (lime and calcium sulphate) and fly ash, as expected. The silica and alumina contents of the bed material indicate that it also contains fragmented sand particles and part of coal ashes. In spite of the fly ash enrichment in E, the Al_2O_3 amount in B and E was practically the same because the diluting effect of the unburnt elutriated coal particles present in E was greater than that due to the exhausted sorbent and the siliceous material contained in B.

Table 3
E and B chemical composition, wt % - Polish coal

	E	B
CaO	12.34	23.54
Al_2O_3	16.30	16.24
Fe_2O_3	4.69	4.41
SiO_2	33.77	42.36
MgO	2.15	2.56
SO_3	1.94	3.76
loss on ignition (at 950 °C)	21.26	2.17

Taking into account that SO_3 is the limiting oxide for the $C_4A_3\bar{S}$ formation both in B and E, only B was used as raw material for the synthesis because of its higher amount of sulphate.

Samples of B were fired at temperatures of 1000°, 1100°, 1150° and 1200 °C. At 1000 °C reactants were practically unconverted and at 1200 °C melting phenomena occurred. The influence of the temperatures of 1100° and 1150 °C on the synthesis is illustrated in Tab. 4.

At 1100 °C $C_4A_3\bar{S}$ as well as $C_5S_2\bar{S}$ (calcium sulphosilicate) and C_2AS (gehlenite) were detected within the fired products even if in small amounts. Increasing the burning temperature caused only a slightly higher consumption of the reactants (especially CaO and $CaSO_4$). Traces of C_2S (dicalcium silicate) and C_3A (tricalcium aluminate) were also detected.

In order to reach the temperature of 1200 °C avoiding the occurrence of a liquid phase, it was decided to add reagent grade alumina (A), a high melting point component. The addition of a source of sulphate (reagent grade gypsum) was also necessary in order to bind in $C_4A_3\bar{S}$ all the Al_2O_3 content.

Table 4
Influence of synthesis temperatures on reactants conversion and products formation (B samples) [o]

	1100 °C	1150 °C
Reactants		
CaO	+ +	+
$CaSO_4$	+ +	+
SiO_2	+ + +	+ + +
Products		
$C_4A_3\bar{S}$	+	+
(oo) $C_5S_2\bar{S}$, C_2AS	+	+

[o] Symbols indicate XRD peaks intensities: + =low; + + =medium; + + + =high.

[oo] These phases can be present alone or together inasmuch as their strongest signals overlap.

Table 5
Conversion of reactants and formation of products (B-A-G sample) °

	1200 °C
Reactants	
CaO	+
$CaSO_4$	+ + +
SiO_2	+ +
Al_2O_3	+ +
Products	
$C_4A_3\bar{S}$	+ + +
(oo) $C_5S_2\bar{S}$, C_2AS	+

° See footnote in Table 4.
°° See footnote in Table 4.

The composition of this ternary system (B-A-G) was: 74% B, 16.2% A, 9.8% $C\bar{S}H_2$, *i.e.* the stoichiometric proportions for exploiting all the available lime to form $C_4A_3\bar{S}$. The XRD results on the B-A-G mixture fired at 1200 °C are shown in Tab. 5.

The ternary mixture showed a greater selectivity towards the desired product, $C_4A_3\bar{S}$, even if substantial amounts of unconverted reactants were still present. Together with $C_4A_3\bar{S}$, $C_5S_2\bar{S}$ and C_2AS, traces of C_2S, C_3A and other calcium aluminates were detected.

Further work is in progress in order to achieve higher conversion and selectivity degrees by means of a suitable choice of heating temperatures and times. Furthermore, the possibility of converting the silica present in the reacting system into dicalcium silicate will be explored.

5.2. Combustion of South African coal

Chemical composition of elutriated (E) and bed (B) materials generated by the South African coal combustion is shown in Tab. 6.

Quartz in E, and lime, anhydrite and quartz in B were the prevailing crystalline phases.

From the comparison of the data listed in Tables 3 and 6, it can be achieved that the enrichment degree in exhausted sorbent for B and in fly ash for E was considerably higher in the case of the South African coal. Moreover, fly ash generated by this coal was remarkably lower in alumina and unburnt coal, and higher in silica. Finally, the SiO_2 content of B was mainly due to the unavoidable sand fragmentation.

Both E and B have an unsatisfactory alumina content but B can give the required lime and sulphate amounts for the $C_4A_3\bar{S}$ synthesis.

It was therefore decided to mix B with reagent grade alumina (A) and to investigate the behaviour of a binary system (B-A) containing 62.5% B and 37.5% A (namely the stoichiometric proportions for combining in $C_4A_3\bar{S}$ all the sulphate).

Table 6
E and B chemical composition, wt % - South African coal

	E	B
CaO	5.39	51.87
Al_2O_3	4.58	1.61
Fe_2O_3	1.51	1.31
SiO_2	75.44	20.60
MgO	1.33	0.82
SO_3	1.41	16.33
loss on ignition (at 950 °C)	8.40	0.13

Samples of B-A were fired at 1000°, 1100° and 1200 °C. The influence of synthesis temperatures on reactants conversion and products formation is shown in Tab. 7.

At 1000° and 1100 °C weak signals of C_2AS, $C_5S_2\bar{S}$ and $C_4A_3\bar{S}$ were detected, while at 1200 °C it was observed a strong reduction of the reactants concentration together with an increased conversion to $C_4A_3\bar{S}$. Other detected products were C_2S and various calcium aluminates.

Future research developments on this system will concern an optimization of both synthesis conditions and raw mix proportioning.

Table 7
Influence of synthesis temperatures on reactants conversion and products formation (B-A samples) °

	1000 °C	1100 °C	1200 °C
Reactants			
CaO	+ + +	+ + +	+
$CaSO_4$	+ + +	+ + +	+ +
SiO_2	+	+	+
Al_2O_3	+ + +	+ + +	+
Products			
$C_4A_3\bar{S}$	traces	+	+ + +
(oo)$C_5S_2\bar{S}$, C_2AS	+	+	+

° See footnote in Table 4.

°° See footnote in Table 4.

6. CONCLUSIONS

The high free lime content and the low degree of pozzolanic activity generally hinder the use of fluidized bed combustion wastes in ordinary Portland and blended cements. It has been demonstrated that special cements based on calcium sulphoaluminate can be obtained through a high temperature synthesis of raw mixes composed by laboratory made combustion and desulphurization wastes containing reactive lime, sulphate and alumina.

Burning temperatures and times as well as raw mix proportions can be optimized in order to obtain cementitious components having satisfactory hydraulic properties.

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Waste Materials in Construction
G.R. Woolley, J.J.M. Goumans and P.J. Wainwright (Editors)

Synthetic aggregates from combustion ashes using an innovative rotary kiln.

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This paper describes the use of a number of different combustion ashes to manufacture synthetic aggregates using an innovative rotary 'Trefoil' kiln. Three types of combustion ash were used, namely:

- incinerated sewage sludge ash (ISSA);
- municipal solid waste incinerator bottom ash (MSWIBA - referred to here as BA); and
- pulverised fuel ash (Pfa)

The fine waste ash fractions listed above were combined with a binder to create a plastic mix that was capable of being formed into 'green pellets'. These pellets were then fired in a Trefoil kiln to sinter the ashes into hard fused aggregates which were then tested for use as a replacement for the natural coarse aggregate in concrete. Results up to 28 days showed that these synthetic aggregates were capable of producing concretes with compressive strengths raging from 33 to 51 Mpa, equivalent to between 73% and 112% of that of the control concrete made with natural aggregates.

1. INTRODUCTION

This project is specifically aimed at using an innovative design of rotary kiln (known as the Trefoil kiln) to provide a solution to two modern day dilemmas which confront both disposers of waste and users of natural aggregates for the production of concrete. The dilemmas are:

- how to overcome the conflicting problems of dealing with the increasing amounts of domestic and industrial wastes and, at the same time, effect a reduction in the numbers of landfill sites being used for disposal; and
- how to limit the use of irreplaceable natural resources and still satisfy the growing demand for aggregate.

The particular waste streams investigated in the project were:

- incinerated sewage sludge ash (ISSA)
- municipal solid waste incinerator bottom ash (MSWIBA - BA); and
- pulverised fuel ash (Pfa)

1.1 MSWI BA

As the reliance on landfill as the primary waste management option declines in the UK more Municipal Solid Waste incinerators (MSWI) will be needed. Depending on the levels of minimisation, reuse, and recycling the number of new incinerators is estimated to be between 28 and 165 (200 000 t/a) [1] in the coming decades. This will produce a large and consistent supply of MSWI Bottom Ash. Such quantities will help to encourage the use of bottom ash (BA) as a construction material. This is a sensible method of utilisation as it avoids the problems and costs associated with disposal and provides an alternative aggregate source. Concern has been expressed over the use of BA in construction due to the metals contamination and the associated expansion when incorporated in concrete [2]. Methods of sintering and vitrification of BA to decrease the availability of toxic elements are well documented [3,4 5,6,7] but energy costs are high and use is limited.

The levels of metal contamination within BA mean that without vitrification utilisation requires some form of encapsulation or covering to prevent the leaching of contaminants into the groundwater. At present the main use of BA is in bound applications to reduce the potential for contaminant release [8,9,10], such applications include: asphaltic concrete, concrete blocks and cementitious sub-bases in roads. Improvements in BA quality can be brought about by washing and or ageing [11], this decreases the mobility of metals by oxidation and carbonation reducing the pH and producing more stable mineral phases.

Evidence from continental Europe (See [12] for example) suggests that BA is a potentially suitable material for some construction purposes. This has been borne out by recent developments in the UK where ash is being used from three incinerators and industry is drawing up guidelines on its use [13].

Satisfactory results have been obtained in previous work on producing a quality aggregate from sintering BA in a traditional rotary kiln [14-17]. The resultant aggregate was used to replace natural coarse aggregate in a number of concrete specimens, which were then tested over a 5-year period for structural performance and long term degradation.

1.2. ISSA

A rotary kiln has been used to produce a lightweight aggregate (LWA) from a mixture of de-watered sewage sludge and clay [18]. This mix was extruded, chopped into pellets and fired in a rotary kiln at up to 1090 °C. Strengths of up to 35Mpa have been achieved from concretes in which this material was used to replace the natural coarse aggregate. A mixture of de-watered sludge and a binder has also been fired in a brick kiln to produce a material which, after crushing, resulted in a hard angular rough textured aggregate with a loose bulk density of 600 – 650 kg/m3 and water absorption of approximately 7% [19,20]

Recent legislation preventing the dumping of sewage sludge at sea [21] from the end of December 1998 has meant that a number of alternatives are being sought by water companies to dispose of the sludge. One such method is incineration which produces a granular ash (ISSA) which itself needs to be disposed of. Currently the majority of the ash is disposed of to landfill, but there has been some recent work undertaken to assess its potential for use as a construction material. A 3 tonne per day capacity plant has been constructed in Tokyo [22] producing a material called 'sludgelight'. In this process the ISSA is mixed with an organic waste and pelletised before being fired in a vertical shaft furnace at approximately 1050°C. The properties, and performance of the aggregate produced were similar to other commercially available lightweight aggregates (LWA). Tay and Show [23] also demonstrated the use of ground ISSA as an ingredient in producing masonry cement.

1.3 Pfa

Pulverised fuel ash has a long history of use in construction. It can be used as a light base material when compacted, and as a pozzolan as it hardens when mixed with lime and water. The inclusion of pfa as cement replacement in concrete increases the workability of the plastic concrete, reduces the heat of hydration and is therefore useful in large structures such as dams. It also increases the long tem strength of the concrete and, by reducing the permeability, leads to an overall improvement in durability [24].

The use of pfa in the production of lightweight aggregate is also well established [see 25]. Lytag is the trade name given to a LWA produced by sintering low carbon (circa 8%) fly ash. The ash is first pelletised on an inclined disc pelletiser with 5 to 10 % water and is then fired on a 'sinterstrand' at a temperature of about 1000°C. The resultant material is open textured with small voids that are interconnected and permeable to water. Lytag has a loose bulk density of approximately 825 kg/m^3, and is capable of producing concretes with strengths in excess of 40MPa. It is a well established material and has been used in a number of large-scale projects such as, for example, the construction of North Sea oil production platforms [26].

2. EXPERIMENTAL WORK

2.1. The Trefoil Kiln

The Trefoil kiln used in this project is much more thermally efficient than a traditional rotary kiln. Traditional rotary kilns consist of a thick steel drum lined with heavy manually laid fire bricks which have a limited life and which need regular maintenance entailing total shut down which can involve weeks of lost production. By contrast, the Trefoil kiln (see Fig 1), which is potentially the only real advance in kiln design for the last 100 years [27], compresses a ceramic fibre insulation between a thin steel alloy hot face and a tensioned thin mild steel cold face to form a cartridge with a triple-lobed cross section. The advantages of such a design include:

- excellent thermal efficiency (an inner kiln temperature of 1200° C and an outer temperature of 60° C);
- a much smaller and lighter structure which does not need costly maintenance or relining and which is easier to manufacture, transport, install, remove and replace;
- much faster heat-up and cool-down periods (50 times quicker than conventional kilns);
- vastly improved responsiveness (operating temperatures can be increased or decreased in minutes); and
- higher load factors.

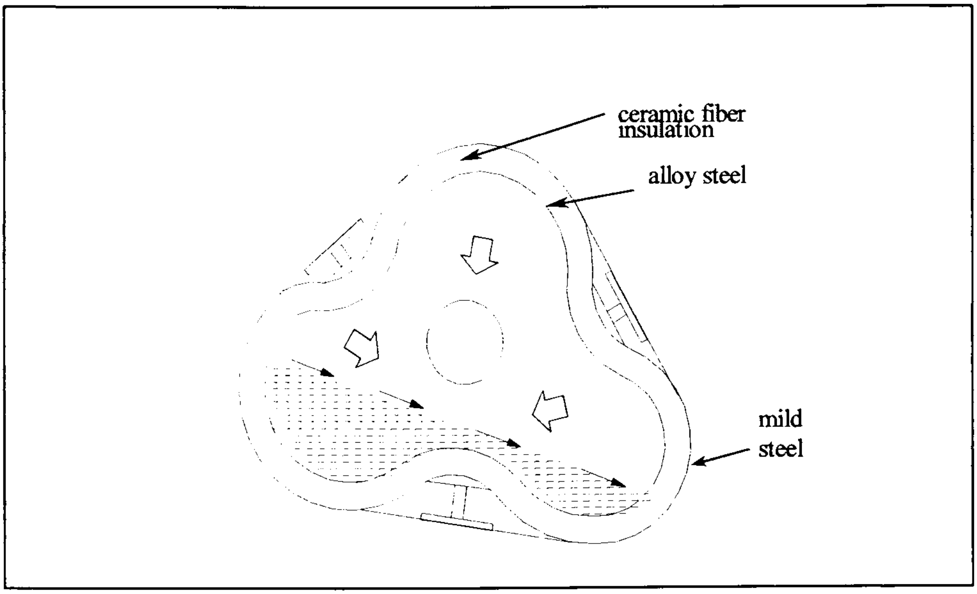

Figure 1. Cross-section of the Trefoil kiln

2.2. Materials

The mineralogy of all three ashes used were similar consisting mainly of silica (SiO_2), alumina (Al_2O_3), iron oxide (Fe_2O_3), calcium oxide (CaO) [19,24,28] with smaller amounts of Cu, Zn, K and other metal oxides. The pfa used had proportionally more silica and alumina than the other two ashes. The ISSA was derived from the incineration of sewage sludge from a plant in the UK. The ash was used in its conditioned state at dry solids content of about 75 % with all the material passing 1 mm. The MSWIBA (referred to here as BA) used was that passing 600 μm obtained from the 0 – 6 mm fraction of a sample taken from a bottom ash recycling plant in the UK. The processing undertaken at the plant consisted of a small amount of size reduction and removal of ferrous and non-ferrous metals. The pfa was obtained as a grab sample from the dry area of a settling lagoon of a UK power station.

2.3. Aggregate extrusion / pelletisation

The first stage in the aggregate production process was to blend the ashes with a binder to enable the mixture to be extruded and pelletised. In this study the binder used was clay, raw sewage sludge or a combination of both. The proportions of the different types of ashes and binders used are shown in Table1. At the time of writing it is not possible, for commercial reasons, to disclose the proportions of pfa and sewage sludge that were used.

Once blended the mixtures were extruded and then pelletised by means of a rotary drum pelletiser that also incorporated a burner drier. The combined action of the drier and the rolling motion of the drum produced a skin on the pellets that aided green pellet strength and created a thin denser outer rim on the fired pellet.

Table 1
Ratio of Ash to Binder in the Aggregates

Aggregate	% Ash	% Binder % Clay	 % Sewage sludge (dry weight)
ISSA 1	63	10	27
ISSA 2	64	20	16
BA 1	82 (< 600 μm)	18	--
BA 2	85 (< 300 μm) 5 (>300 < 600 μm)	10	--
Pfa	✓	✓	✓

2.4. Aggregate firing

Firing of the synthetic aggregate consisted of two stages; the first is known as the 'burnout' stage where the carbon content of the ash / binder mix is allowed to combust (burnout) at a temperature below that where the inert material in the pellet begins to sinter. From previous experience it was known that this stage can take between 5 and 40 minutes and occurs between 700°C and 800°C, depending on the amount and type of carbon (organic material) present and the internal structure of the pellet. The carbon content of a lightweight aggregate produced from pfa needs to be below 4% to conform to BS 3797 [29] and it was considered appropriate to adopt this figure in this study. To ensure that this 4% level was reached before the sintering stage begins samples of the aggregate were taken at various times during burnout and analysed for the carbon content. It was assumed that the remaining carbon would be burnt during further firing and could provide a volatile material for the production of voids during sintering, thus helping to give a lightweight structure to the pellet. All aggregates produced were tested for relative density and water absorption in accordance with BS 812 [30].

2.5. Casting

A number of different concrete mixes were made in which the natural coarse aggregate was replaced with the synthetic aggregates. The mix ratios used together with the free water / cement ratios and the workabilities are shown in Table 2. All mixes were designed to have nominally the same volume proportions with adjustments being made on the basis of loose bulk density. All the sintered ash aggregates were soaked in water prior to casting to ensure that they were in a saturated surface dried condition. Cubes were cast from all mixes for measurement of compressive strength in accordance with BS1881 [31].

Table 2
Mix Ratios (by weight of cement) for all concrete specimens

	ISSA 1	ISSA 2	Pfa	BA 1	BA 2	Control	Lytag
Coarse aggregate	2.21	2.34	2.20	2.52	2.37	3.64	2.47
Sand	2.23	2.23	2.23	2.23	2.23	2.23	2.23
OPC	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Free water : cement	0.55	0.55	0.53	0.53	0.53	0.53	0.53
Slump (mm)	20	50	50	95	135	20	10

3. RESULTS

3.1. Aggregate Properties

The densities and water absorption figures for the aggregates produced from the combustion ashes are shown in Table 3, where they are compared with natural aggregate and with Lytag. The Relative Densities range from 1.6 to 1.9 which are significantly lower than the natural aggregate at 2.6 and similar to Lytag at 1.7. All have dry bulk densities below 1000kg/m^3, which classifies them as lightweight aggregates. The water absorption figures do not all follow the expected trend of high absorption corresponding to low density. Two of the aggregates (BA2, ISSA2) have low densities 985 and 830 kg/m^3 respectively and relatively low absorption figures (when compared to Lytag) of 4.5% and 8.1% respectively. This would suggest that the pore structure is more segmented in these two aggregate types than in the others. A closed pore structure is considered more beneficial because it is likely to result in higher strength and lower shrinkage than with a more open structured aggregate of similar density.

Table 3
Aggregate Properties

Aggregate	Dry loose bulk density kg/m^3	Loose bulk density (SSD) kg/m^3	Relative density (SSD)	24 Hour Water Absorption (% dry mass)
BA 1	920	1036	1.9	12.7
BA 2	985	1034	1.9	4.5
pfa	816	960	1.7	17.7
ISSA 1	630	730	1.6	15.5
ISSA 2	830	900	1.7	8.1
10 mm Nat.Agg.	1510	1520	2.6	0.8
Lytag	780	875	1.8	12.3

Further work is on going to study in more detail the microstructure of the aggregates and to develop a model to be able to predict this structure from knowledge of the constituent materials and kiln firing conditions.

3.2. Concrete workability

The workabilities (slump) of all seven mixes made to nominally the same water / cement ratios of 0.53 are shown in Table2. All mixes, with the exception of the control mix, had similar densities and it is reasonable therefore to make comparisons between the Lytag mix and the remainder of those mixes made with the synthetic aggregates manufactured in this study. Using any of the synthetic aggregates as a coarse aggregate replacement leads to an increase in workability when compared with Lytag. In the case of the two mixes made with the bottom ash aggregates (BA1,2) the increases are significant from 10mm to between 95 and 135mm respectively. All the aggregates produced in this study tended to be slightly more rounded and smoother than Lytag which would account for some of the increase, but no reason can be given at this stage for the significant increases observed with the two bottom ash aggregate mixes.

3.3 Compressive strength

Unfortunately at the time of writing strength results are only available up to the age of 28 days and these are shown for all mixes in Figure 2. In addition the ratio of the 28 day strengths of the mixes compared to both the Lytag and the natural aggregate control concretes are shown in Table 4.

Table 4
Strength of sintered ash aggregate concrete compared to control and Lytag concrete.

Aggregate	% of Lytag concrete 28 day strength	% of Control concrete 28 day strength
BA 1	79	73
BA 2	95	88
PFA 1	98	90
ISSA 1	90	84
ISSA 2	120	112

The compressive strength results for all the different aggregate types are encouraging, in most cases they are similar in performance to both the control mixes and differ little from each other. Only two mixes show any significant differences in trend, that made from the incinerated sewage sludge ash (ISSA 2) and that made with the bottom ash (BA 1). In the case of the former the 28 day strength is 20% higher than with Lytag (51MPa cf. 42Mpa) and 12% stronger than even the natural aggregate control (51Mpa cf. 45Mpa). Comparing ISSA 2 with ISSA 1 (Table 1) would indicate that the addition of 10% extra clay as the binder at the expense of the sewage sludge is beneficial in terms of compressive strength (Fig. 2) and water absorption (Table3). Interestingly the reverse appears to be true in the case of those aggregates made with bottom ash where the aggregate with the lower clay content (BA 2) performs better than BA1 containing 8% more clay. The 28 day strength of the mix made with the BA 1 aggregate is the lowest of all at 28Mpa which is 21% and 27% lower than the Lytag and natural aggregate control mixes respectively.

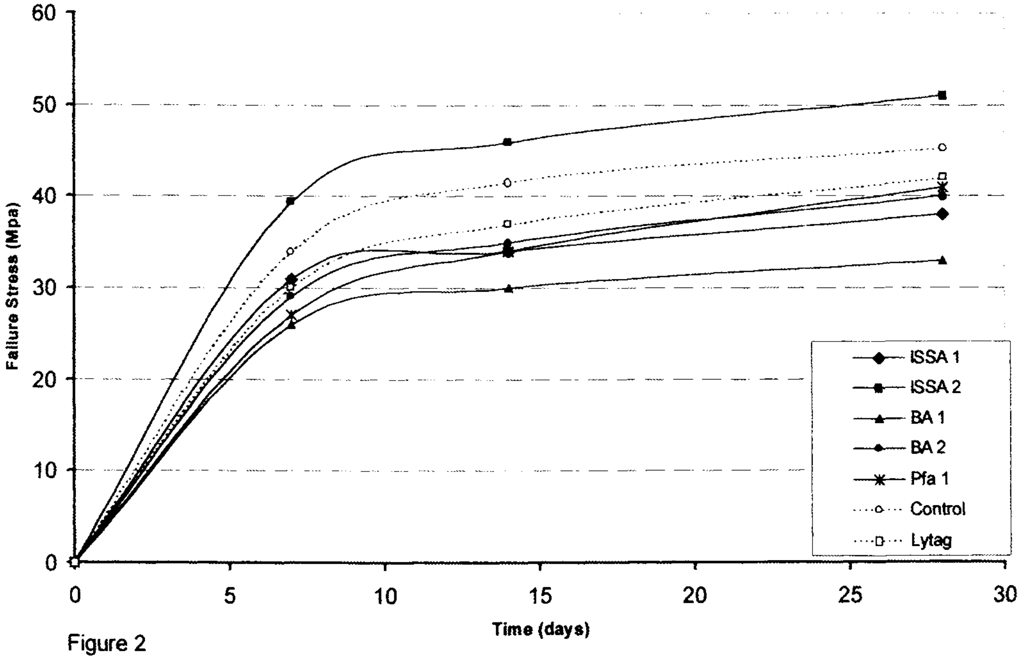

Figure 2
Compressive Strengths of Synthetic Aggregate Concrete.

3.4 Future work programme

These results show that concretes with reasonable strengths can be made with synthetic aggregates produced from any of the waste streams investigated, but more work is needed to find the mix proportions (in terms of ash and binder contents) to give the optimum performance from the aggregates. Although the strength results obtained to date are satisfactory, much longer term data is needed to determine whether or not there are any potentially deleterious reactions taking place between the aggregates and the cement paste. The work programme currently underway is designed to address these questions as well as provide important information on the leaching characteristics of the synthetic aggregates. Future planned work will also look at other properties of concretes made with these aggregates such as: permeability, elasticity, shrinkage and creep.

4. CONCLUSIONS

The results of the tests reported here have shown that it is possible to successfully manufacture synthetic lightweight aggregates from the combustion ashes derived from the incineration of: sewage sludge, municipal solid waste and pulverised coal (pfa). The ashes were combined with a binder, extruded to form pellets and then fired in a Trefoil rotary kiln to produce synthetic lightweight aggregate. Concretes made with the synthetic aggregate achieved 28 day strengths of between 33 and 51 Mpa compared with 45 and 42 Mpa for the natural aggregate and Lytag aggregate control mixes respectively. Further work is being undertaken to establish the leaching characteristics of the aggregates and the optimum mixture proportions to give the most desirable aggregate properties.

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Waste Materials in Construction
G.R. Woolley, J.J.M. Goumans and P.J. Wainwright (Editors)

The Properties of Recycled Precast Concrete Hollow Core Slabs for Use as Replacement Aggregate in Concrete

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Summary

Waste concrete from prestressed precast hollow cored floor units has been recycled for use as replacement aggregate in concrete (RCA). Waste concrete blocks were crushed to −14 mm using cone, impact and jaw crushers. All produced acceptable physical and mechanical properties, although the impact crusher was best suited in most cases. The water absorption of the RCA was 3 to 4 times greater than natural limestone and river gravel used for control purposes. The fine RCA was at the coarse end of the British Standard limit. Concrete made using zero, 20% and 50% replacement of coarse and fine RCA had increased workability at 20% replacement, but this reduced considerably at 50% replacement. Compressive strength of concrete made with RCA was generally within ±5 N/mm^2 of the control value of 62 N/mm^2. RCA from the cone crusher produced the highest strengths. The main conclusion is that concrete made with up to 50% replacement of both coarse and fine RCA appears to be comparable with natural aggregate concrete in terms of workability and compressive strength.

1 Introduction

The precast concrete hollow core floor industry produces a considerable amount of wasted concrete elements, due mainly to the manufacturing processes and in part to natural wastage at the ends of the casting beds. Figure 1 shows how prestressed hollow core units (hcu) are manufactured by extrusion or slip-forming through a machine on long beds, typically 100 m in length x 1.2 m wide. Waste material is made at the beginning and end of each bed, typically 0.3 to 0.4 m^3 per casting. After detensioning the units are cut to length. Waste material is therefore made if the cumulative length of the units does not equal the net cast length. This can be between zero and 0.5 m^3 per casting. The total waste generated in the UK is around 5% of the production.

Waste material from hcu is high grade and uncontaminated material . The parent concrete is hard and of compressive strength between 50 to 80 N/mm^2. It is manufactured from Portland cement, and from clean and reliable sources of 10 mm to 14 mm limestone or gravel. The grading of the coarse and fine aggregates is carefully controlled, and together with a

Figure 1. End line waste of hollow core slab units

water cement ratio of around 0.3 the resulting concrete is of a high density and low porosity. It is also extremely brittle and will fracture into flaky shapes with acute edges. In commercial crushers large amounts of fine aggregate are produced, which cause concern for the reintroduction to hcu manufacture. To date recycled coarse aggregate (RCCA) has been considered at replacement levels of up to 20% while the recycled fine aggregate (RCFA) only up to 10%.

A recent project (P.I.T)(1) conducted by the member companies of the UK's Precast Flooring Federation has found that the effects of using 20% of RCCA + 10% of RCFA in precast concrete are small. They indicated that the differences recorded in compressive and flexural strength were mostly less than the variability of the test. Also they reported that shrinkage and creep measurements were more consistently affected but still fairly small and should not contravene any specification requirements. Differences resulting from the crushing method were not investigated.

To complement this work, this present research aims to study the properties of recycled concrete from hcus crushed using three different methods - cone, jaw and impact crushers. Commercial hcus, manufactured by Richard Lees Ltd. using the *Spiroll* extrusion technique, were obtained for this study. The mix content for the parent concrete is given in Table 1. The resulting crushed material was first separated into coarse (10 mm and 14 mm) and fine (≤ 5 mm) fractions. It was tested for those properties which are important to the reintroduction of RCA into hcu production, namely grading, water absorption, density, shape, ten-per-cent fines value, workability and strength. The recycled aggregates were also tested in concrete mixes in which the aggregates in a 'reference' mix were substituted with varying

Table 1: Mix content for the parent concrete (hcus)

14 mm	10 mm	Sand	Cement Class 52.5N	Pozzolan	Water
340 Kg	440 Kg	500 Kg	200 Kg	60 Kg	50 Kg

proportions of recycled concrete aggregate. The chosen percentage replacement was 20% and 50% - the former represents a typical limit for RCCA proposed in P.I.T project, and the latter is made deliberately large in order to investigate the sensitivity of the said mechanical and physical properties.

This paper reviews the determination of mechanical and physical properties of RCA alone. The results are compared for compliance with the relevant British Standards. The paper also presents the results of tests carried out on fresh and hardened concrete made with natural aggregates and RCA.

2 Crushers

To enable discussion on the properties of RCA obtained from the crushing operation, it is first necessary to review this in relation to crushing hardened concrete. It should be noted that most crushing machines were developed for crushing rock into sizes with equivalent diameters of 50 mm or greater. In some cases special modifications to the orifice had to be made to produce RCA of 14 mm size.

2.1 Cone Crusher

Cone crushers are one of the major categories of gyrating crushers, which have developed into being one of the most important types of machine in use in quarrying(2). The principle is shown in Figure 2. It uses a repeated compression action with fixed and moving crushing members. The long stroke and high speed agitate the feed in its passage through the chamber. At the lower extremity of the crushing chamber the faces of the two crushing member are so shaped that they are parallel for a section, resulting in the larger pieces being assured of having at least one dimension equal to, or less than, the setting, quoted as closed-side setting (CSS) when properly fed and certainly all products less than twice the CSS.

In the operation to crush hcu, the size of the feed was up to 350 mm and the CSS was set at about 14 mm. The resulting RCA was acceptable in appearance and seems to be slightly towards flaky and elongated in shape. There is no distinguished dust on the coarse particles. The amount of cement paste attached to the virgin aggregate was quite large.

2.2 Jaw Crusher

Jaw crushers are also commonly used in quarries. Its principle could be summarized in that the feed is subjected to repeated pressure as it passes downwards and is progressively reduced in size until it is eventually small enough to pass out of the crushing chamber. See Figure 2. The size of machine also affects its speed which decreases as the crusher size increases. The angle between the crushing faces is normally between 19° and 22°. This angle is set to allow the crushing force to be transmitted to very hard materials without a tendency for the feed to rise itself out of the crushing zone and so cause abrasive wear to the liners. The setting is usually measured as a CSS, i.e. when the jaws are at their closest position, and some times as open side setting with the jaws at their greatest distance apart.

In the operation to crush hcu, the size of the feed was nominally 25mm and the CSS was set at about 15mm. The resulting RCA was good in appearance and seems to be slightly elongated with no distinguish dust on the coarse particles. The amount of cement paste attached to the virgin aggregate was quite large.

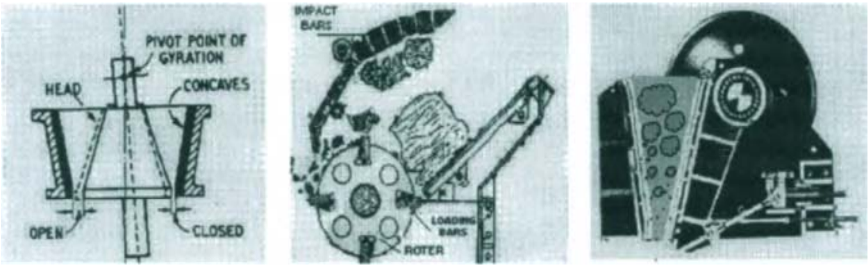

Figure 2: Cone Crusher (left), Impact crusher (middle) and Jaw Crusher (right).

2.3 Impact crusher

Impact crushing could be described as impact breaking since the feed is fragmented by kinetic energy introduced by a rotating mass (the rotor) which projects the material against a fixed surface causing it to shatter causing further particles size reduction. The process causes the material to break along its natural cleavage planes and this yields a good product shape free from stress. The rotor speed is fundamental to the breaking process where the higher speed the higher reduction factor; the size of the material fed into the crusher to the size of the finished product. In the operation to crush hcu, the size of the feed was nominally 500mm. The opening size was 700mm x 500mm with 1800 RPM rotation. The resulting RCA was less elongated towards rounded shape with acute edges. There was a distinguish dust on the coarse particles. The amount of cement paste attached to the virgin aggregate also was quite large.

2.4 Summary of Crushing Operations

- In visual appearance the RCA produced from the three crushers seems to be relativly the same in apperance but slightly better shape could be seen from impact crusher.
- The amount of fines obtained from the crushers was cearly high for impact crusher then followed by cone and then jaw.
- The speed at which the quantity of RCA was produced by the different crushers was convenient. It is qiute high for the imapct crusher while the cone and jaw were relatively the same but slower than the impact.

3 Physical properties of Recycled Concrete Aggregate (RCA)

3.1 Density and Water Absorption

The presence of internal pores in the crushed particles has an influence on the porosity and absorption properties of RCA. These properties have a major effect on the workability and durability of concrete with a low water-cement ratio, especially used in hcu production. They also have an influence on the bond to hydrated cement past as well as the concrete resistance to freezing and thawing, and to a lesser extent carbonation. Water absorption and density were measured (to BS 812, Part 2, 1995(3)) for the RCA and natural crushed carboniferous limestone (obtained from Tarmac Quarry Products – Retford). The results given in Tables 2 and 3 are the mean of 2 samples.

3.1.1 Density and Water Absorption of Coarse RCCA

It was expected for the RCCA to have a higher water absorption and lower density than the natural limestone because of the cement mortar attached to it. The results given in Table 2 show that the water absorption for 10 mm and 14 mm RCCA is around four times greater than that of the limestone with similar size. Table 3 shows that the surface saturated density (SSD) is between 4% and 7% lower than that of natural limestone with similar size.

Concerning the effects of different crushing methods on water absorption and density, there were no distinctive differences nor trends. This might give an indication to that there is no significant difference on the amount of cement mortar attached to the RCA obtained from the three different crushing machines. In other words, these crushers (if the fed materials are identical) could produce RCCA with approximate close percentages of attached mortar to the aggregate particles. (This could not be considered as a definite conclusion as other methods need to be used to measure accurately the amount of attached mortar to the RCA.)

3.1.2 Density and Water Absorption of Fine RCFA

The water absorption for RCFA is higher than that for natural river gravel sand. This is also due to the attached mortar. The results given in Table 2 show that the water absorption for RCFA is around three times greater than that of the natural gravel sand of similar maximum size and grading profile. Table 3 shows that the surface saturated density (SSD) is 9% lower than that of natural gravel sand of similar size. There is no significant difference between the values of water absorption for RCFA obtained from the different crushing methods. This also probably limits the influence of the crushing machines on the amount of cement mortar attached to RCFA.

Table 2. Water absorption of RCCA and RCFA

Aggregate type	Crusher	Fine ≤ 5 mm	Coarse10 mm	Coarse14 mm
Recycled	Cone	6.8 %	4.6 %	4.4 %
Recycled	Impact	5.8 %	6.0 %	4.1 %
Recycled	Jaw	6.7 %	5.3 %	4.9 %
Limestone	-	-	1.3 %	1.1 %
Gravel sand	-	1.7 %	-	-

Table 3. Surface Saturated Density of RCCA and RCFA (kg/m^3)

Aggregate type	Crusher	Fine ≤ 5 mm	Coarse10 mm	Coarse14 mm
Recycled	Cone	2387	2416	2434
Recycled	Impact	2385	2461	2484
Recycled	Jaw	2448	2426	2439
Limestone	-	-	2641	2646
Gravel sand	-	2627	-	-

3.2 Flakiness Index

A particle is considered to be flaky if its thickness is less than 0.6 times the mean sieve size of the size fraction to which it belongs (BS 812, Part 105.1, 1989[(4)]). BS 882, 1992[(5)] limits the content of the flaky particles to less than 40% for crushed aggregate and not less than 50% for natural gravel. This limitation is recommended in order to avoid entrapped water and air lying beneath flaky aggregate since this could lead to a deteriorating effect on the concrete by affecting its workability.

Values for the flakiness index of the RCCA are given in Table 4. The results are the mean of 2 tests. The data are markedly different for each type of crusher, but are much lower than the BS 882 limit. It was found that the impact crusher has the lowest flakiness index, producing about 60% and 40% less flaky recycled aggregate than the cone and jaw crushers, respectively. The result for the cone crusher is slightly worrying, especially in relation to acute edges causing a large reduction in the ten-per-cent fines load.

3.3 Angularity Number

British Standard BS 812, Part 1, 1975[(6)] defines the angularity number (AI) as 67 minus the percentage of solid volume in a vessel filled with aggregates in a specified manner. The higher the number the more angular is the aggregate and less able to compact. The method is not popularly used, but nevertheless provides a useful indication of the ability for aggregates to compact. The size of coarse aggregate used in these tests was 10-14 mm. The results are the mean of 2 tests.

The results given in Table 4 indicate that the shape of the RCA produced by the cone and impact crushers was bordering near the end of the acceptable range, i.e. AI = 9 to 11, whilst the natural limestone and jaw crushed RCA was within the desirable range of AI = 3 to 6. According to Kaplan[(7)] there is an inverse correlation between AI and the compaction factor (CF), a result which is confirmed in Figure 6 where the CF for the cone crushed RCA replacements is considerable lower than for all other cases. (The implications on mix design, in terms of the required quantity of mixing water to achieve a given compaction for different RCA replacements, is presently under investigation.)

Table 4: Flakiness Index & Angularity Number for RCCA Derived from Different Crushers

RCCA obtained from	Impact	Jaw	Cone	Limestone	BS Limits
Flakiness Index	9%	15%	21%	7%	≤ 40%
Angularity Number	9	6	11	3	*
Ten Percent Fine Value %	170	160	110	150	*
Aggregate Impact Value KN	23	24	25	20	*

* No BS data, but generally considered to be in the range 0 – 11.

3.4 Grading of RCA and Natural Aggregate

Grading was carried out according to BS 812:Part 103:1985. The grading of the RCA were compared with BS 882, 1992 as well as with natural coarse and fine aggregates. The grading curves are shown in Figure 3. All RCCA grading complied with BS 882, 1992 for single sized aggregate, although the gradings for the jaw and cone crushed RCA lie closer to the BS limits than the impact crushed RCA and the natural aggregate. However it would possible to easily adjust the crushing and sieving operation to produce better grading if time had permitted. The gradings are extremely concentrated owing to the previous separations.

Figure 4 presents the gradings for RCFA and river gravel within the limits of the BS 882, 1992 coarse category. It was found that the grading of the RCFA complied with these limits with one exception, viz. jaw crushed RCA passing the 2.36 mm sieve. The RCFA does not comply with the medium category. As expected the natural river gravel complies with the medium category.

The RCFA has a rather coarse grading with only about 20% passing the 600μm sieve, as opposed to the more usual figure of 30% to 35% in quarried sands. This has a significant effect of mix design as the proportion of fine aggregate required to maintain constant workability would need to be considerably increased, typically by about 20%. The proportion of fines passing the 300μm sieve is more than desirable, although the dust was removed from the RCFA during the screening process during crushing.

4 Mechanical Properties of RCA

It is well known that it is difficult, and often meaningless, to test the compressive strength of individual particles of aggregate, and that the most common method is to compact aggregates in bulk or use other indirect methods such as the ten percent fines value (TFV) test. Because the RCA in this project was obtained from a parent concrete of known strength, it was considered unnecessary to measure the compressive strength of the RCA. However, because of the varied shape and uncertain effects of the angularity or flakiness of the RCA, a TFV test was carried out. An aggregate impact value (AIV) test was also carried out for completeness. The TFV test was carried out according to BS 812, Part 111, 1990(8) and AIV test according to BS 812, Part 110, 1990 (9). The tests were carried out on 14 mm coarse RCA size. The results are the mean of 2 tests.

4.1 Ten Percent Fines Value (TFV) of RCCA

Considering the origin of the RCCA, which is identical, this test showed some differences between the crushing machines as shown in Table 4. BS 882:1992 limits the minimum values for TFV when the aggregate used for (a) heavy duty floor 150 kN, (b) wearing surface 100 kN, (c) other uses 50 kN. Based on the assumption that the proportion of RCCA is not likely to exceed 50% replacement, this would qualify the RCCA obtained from impact and jaw crusher to be used in any type of concrete, and exclude the cone crushed RCCA from heavy duty floors. However, it is not known what overall effect mixing RCA with natural aggregates would have on wear.

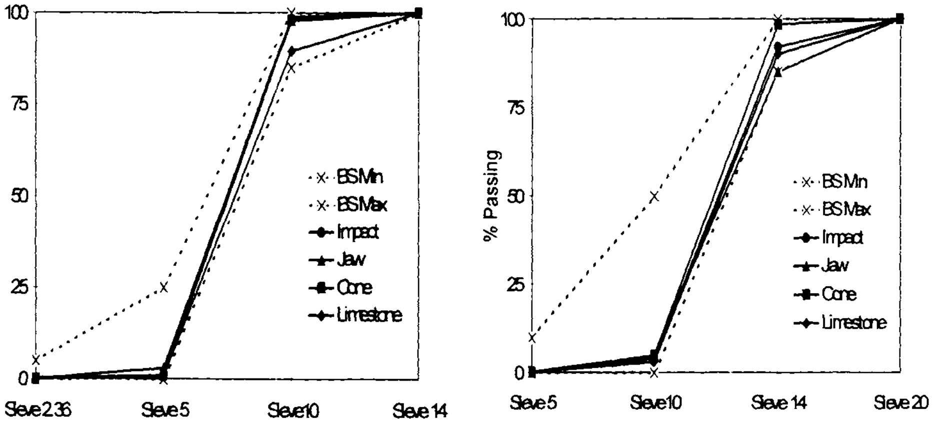

Figure 3: 10 mm, 14 mm Single Size Grading Curves for Natural Limestone and RCCA

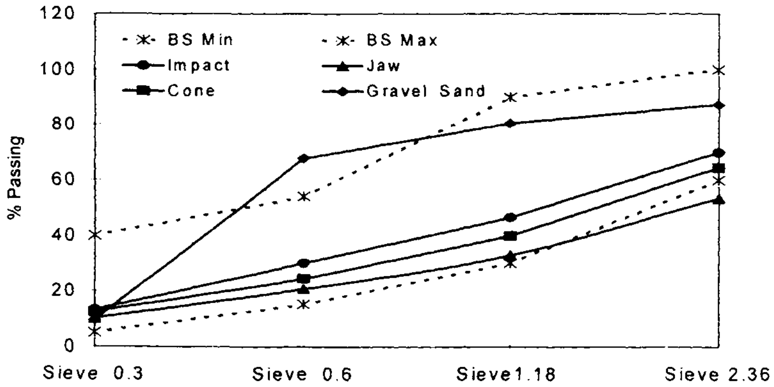

Figure 4: C-Limit Grading Curves for RCFA and Natural River Gravel

4.2 Aggregate Impact Value (AIV) of RCCA

The results shown in Table 4 reveal that the values are almost identical for the RCCA that derived from three different crushing methods, around 24%. The natural limestone value is 20 %. BS 882:1983 limits the maximum values for AIV when the aggregate used for (a) heavy duty floor 25%, (b) wearing surface 30%, and (c) other uses 45%. As with the TFV, assuming a maximum RCCA replacement of 50% all aggregates are suitable for all the above conditions.

5 Fresh Concrete Properties

Specimens were manufactured in the laboratory to determine the workability and compressive cube strength of concrete made from natural (called the 'control' mix) and partially replaced RCA. In all cases the following basic mix proportions were used:

Ordinary Portland cement type 52.5 N	405 kg/m^3
14 mm Coarse aggregate (SSD)	670 kg/m^3
10 mm Coarse aggregate (SSD)	445 kg/m^3
Fine aggregate (SSD)	710 kg/m^3
Water	170 kg/m^3

Mixing complied with BS 1881, Part 125, 1986(10), viz dry mixing for 30 second; 1/3 water added; mixing 2 minutes; standing 10 minutes; cement added; mixing 30 second; remaining water added; mixing 2 minutes. Workability tests were carried out within 5 minutes after mixing. Concrete cubes of 100 mm dimension were made, cured and tested according to BS1881, Part 103, 1991 using a vibrating table to compact the concrete. The replacement proportions of RCA were chosen as 20% and 50%. The former represents a typical limit for RCCA proposed in P.I.T project. The latter was chosen because this is thought to be an extremity worthy of consideration in studying the sensitivity of concrete made with such high replacements, especially for the fine aggregate. The replacement was made for (i) coarse aggregate alone, (ii) fine aggregate alone, and (iii) coarse and fine mixed.

5.1 Workability

The methods used were slump according to BS 1881, Part 102, 1991(11) and compacting factor (CF) according to BS 1881, Part 103, 1991(12). Although the slump method is crude, it is an easily understood measurement of workability and therefore used here. The CF method gives a better understanding of workability. The results shown in Figures 5 and 6 are the mean of 3 samples.

5.1.1 Slump Measurement

The results are shown in Figure 5. The target slump for the control mix was 60 mm. The general trend is an increase in slump as the replacement RCA increases up to 20%, which is followed by a decrease at 50% replacement. The exception is in the case of RCCA replacement where the slump increases at replacement levels greater than 20%.

The effect of the different crushing methods on the coarse and fine RCA is confusing and contradictory. Changes in the slump for RCFA are greatest of all, especially for the cone and jaw crushing methods. RCFA crushed in this manner have greater water absorption (Table 2) so one would have expected a reduction in slump, which is not seen until the replacement is 50%. The effect of grading, in particular the low fraction passing the 600 μm sieve, would suggest a reduction in workability as the replacement RCFA increases for a fixed ratio of fine-coarse aggregate.

For the RCCA, it is the impact crushing method which sees the greatest change. This confirms the results from Table 4 where the RCCA obtained from the cone crusher gave the greatest angularity and therefore its effect on workability would be greater as more bleed water might be retained. However, it contradicts the water absorption result (Table 2) where the impact crushed RCCA had the greatest absorption value, suggesting a reduction in slump. It appears that there are many factors influencing these results.

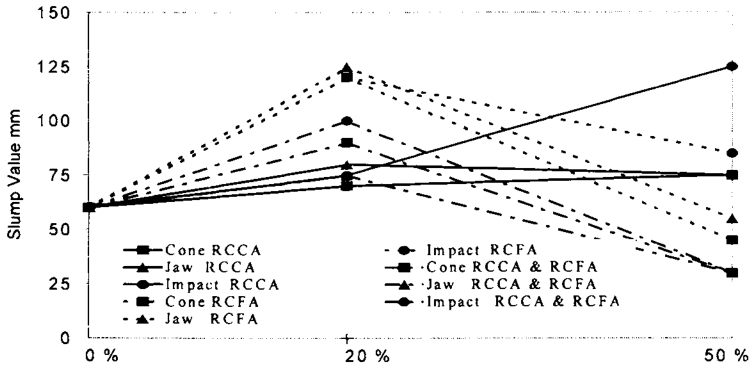

Figure 5 : Slump values for concrete with different replacement percentages) of RCA obtained from different crushers

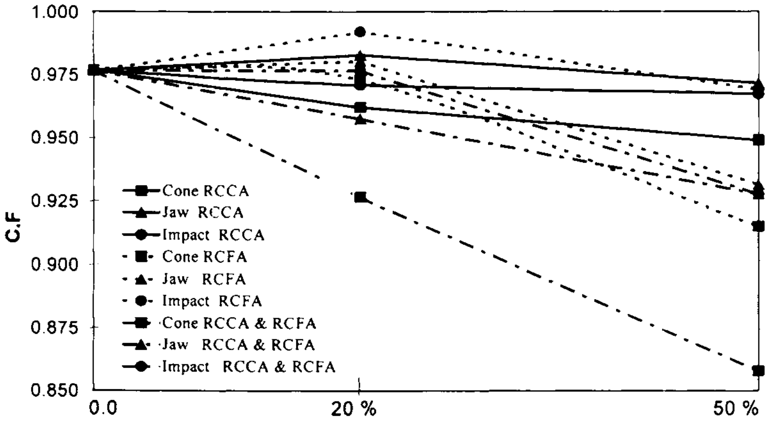

Figure 6: Compacting factor values for concrete with different replacement percentages of RCA obtained from different crushers

5.1.2 Compacting Factor (CF)

The results are shown in figure 6. There was no target CF for the control mix although published literature would suggest that for an aggregate/cement ratio of 6 and a slump of 60 mm, the CF should be about 0.96. The general trend is similar to the slump results. The exception is that there is very little change in the jaw and impact crushed RCCA. The influence of the crushing method appears to be more consistent than in the slump results – the CF for cone crushed RCA is considerably lower in all cases. This is as expected from the angularity tests (Table 4) where the RCCA was found to be angular.

The effect of replacement RCFA on the CF factor is as expected, i.e. a reduction in CF from 0.975 to 0.93 (average), owing to increase water absorption and reduced density. The effect of grading, in particular the low fraction passing the 600 μm sieve, would suggest a reduction in CF as the replacement RCFA increases. A change in CF from 0.975 to 0.93 is

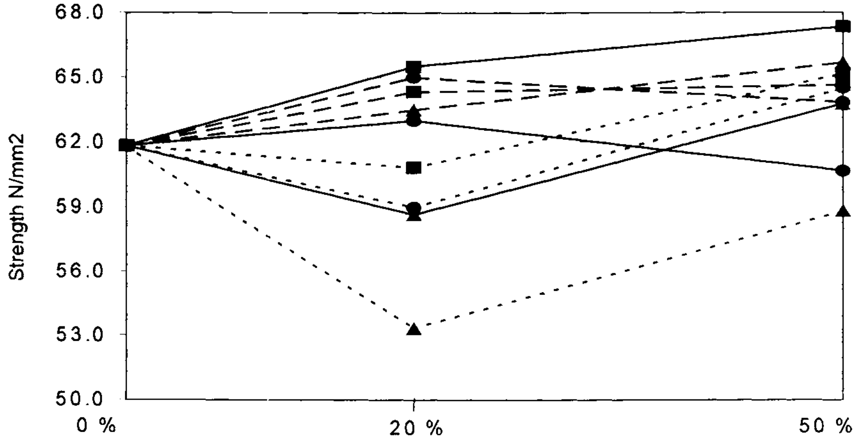

Figure 7 : 28 days Compressive strength of concrete with different replacements of RCA derived from different crushers (notations as Figure 6)

quite considerable and could be interpreted as a three fold increase in the mixing air content.

The results for the RCCA are more encouraging with little change in the CF, with the exception of the cone crushed RCCA which we have already noted as being rather angular. The implications for compacting concrete are therefore less onerous (but still important). The effect of particle size is not conclusive owing to the small variations in grading (Figure 3).

6 Strength of Concrete with Natural Aggregates and RCA

The strength of concrete reported in this paper is compressive cube strength, according to BS 1881, Part 116, 1991⁽¹³⁾. The target strength for the control mix reached about 60 N/mm^2; results are shown in Figure 7. In all cases of different types and proportions of replacement RCA the mix using RCA from the cone crusher achieved the highest compressive strength. This contradicts all previous expectations that the cone crusher gives the poorest performance in terms of aggregate properties (e.g. high water absorption, low density, high flakiness) and workability (e.g. lowest CF). It is therefore clear that the compaction of the concrete has an important effect on the final product.

7 Discussion

Different crushing methods have an influence on the properties of recycled concrete aggregate. Physical properties, specifically shape and texture, appears to be effected mostly and showed some variance related to each type of crusher. It was found that one crusher performed well in some properties and shows some disadvantages in others.

All crushers produced RCA with acceptable strength and shape (See Table 4). However, the impact crusher appears to be the most suitable overall by producing RCA with better shape and strength, then followed by the jaw and then cone crusher. There is no distinctive influence of the crushing methods on the water absorption and density for recycled concrete aggregate (Table 2 and 3). However, concrete made with RCA produced by the cone crusher achieved the greatest compressive cube strengths – several of which exceeded the control mix using natural limestone and river gravel sand.

Comparing the coarse RCCA with natural limestone aggregate, the RCA showed similar (or even better) properties especially for shape and strength. However the RCCA will absorb about 4 to 6 times more water than the natural limestone aggregate. All RCCA appear to have a reasonable grading comparing with the British Standard and is similar to that for natural limestone aggregate. However, it should be noted that the impact crusher has one major disadvantage, which is that it has a large reduction factor (from the feed to the output) and consequently it produces large amount of fine aggregate than coarse aggregate. This agrees with Boesman's findings(14).

The fine RCFA was considerably coarser than the natural river gravel, and technically did not comply with the BS coarse category limits, failing at the 2.36 mm sieve size only. The effect of a smaller fraction of RCFA below 600 μm may have a significant effect on the desired mix proportions to keep workability constant. In spite of the generally poor characteristics of the RCFA in terms of porosity and grading, the effect on the workability and strength of the resulting concrete was, in 8 out of 9 cases, not deleterious, even at 50% replacement.

8 Conclusion

Waste concrete from mature prestressed concrete hollow cored floor units, produced by proprietary extrusion techniques, and having compressive strengths of about 60 N/mm^2 have been recycled for use as replacement aggregate in high strength concrete. The waste concrete was crushed to –14 mm using three different types of crushers – the cone, impact and jaw crushers. The recycled material was separated into fractions of 14 mm, 10 mm and –5 mm, and tested for physical and mechanical properties relevant to use in concrete. Concrete was then made using zero, 20% and 50% replacement of recycled coarse (RCCA), recycled fine (RCFA) and mixed (RCCA+RCFA) aggregates. The control mix was made using natural limestone coarse and river gravel fine aggregates. The concrete was tested for slump, compaction factor and compressive cube strength.

The following may be concluded:

- All three crushers produced acceptable shape and strength of RCCA. Some properties are competitive to that of natural limestone aggregate except for water absorption, which is 4 times greater.
- RCFA was much coarser than river gravel and just complied with the British Standard coarse grading limits. Its water absorption is 3 times greater than the gravel.
- The impact crusher performed best with regard to most aggregate properties, e.g. flakiness, strength and water absorption, but has a disadvantage in producing a large amount of fine-to-coarse RCA.

- Concerning shape and strength, RCA showed similar properties, and in some cases better, than the conventional limestone aggregate.
- The slump value of fresh concrete made with RCA varied widely depending on the percentage and type of replacement, and the type of crusher, a fact which may be linked to the angularity of the RCCA.
- The compaction factor of fresh concrete made with RCA was more consistent and logical, and showed the problems encountered with using angular RCCA produced by the cone crusher.
- Compressive strength of concrete made with RCA were generally within ±5 N/mm^2 of the control value of 62 N/mm^2.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Effects of foundry dusts on the mechanical, microstructural and leaching characteristics of a cementitious system

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The disposal or recycling of industrial wastes has been an important and complex issue for the last 20 years. Hydraulic binders have been widely use to treat and/or reuse waste materials. Synthetic wastes are commonly studied but it does eliminate synergistic waste/binder interference effects that can result from real wastes, which are often composed of complex chemical compounds.

The objective of this research was to investigate the possibility of reusing waste from the foundry industry. For this purpose, 3 wastes from foundry plants have been selected based on their common metal contaminants. Therefore, the objective of this paper is to investigate the effects of the major metal contaminants, Pb, Zn and Mn, on the mechanical (setting time, unconfined compressive strength (UCS)) microstructural (X-ray diffractometry (XRD)) and leaching characteristics (acid neutralisation capacity test) of the solidified waste materials. The results showed that the addition of the wastes induced a retardation of the setting time, which is believed to be due to the presence of Zn, which is a known retardant. It was also revealed that, at equal water/cement ratio and after 28 days, the UCS of most waste products is within +10% of the controls. The mineralogical composition, as depicted by the XRD results, was particularly affected as shown by the clear increase of the non-hydrated products. Finally, the addition of the different wastes was shown to have no effect on the buffering capacity of the solidified products.

1. INTRODUCTION

The disposal or recycling of industrial wastes is an important and complex issue. Hydraulic binders have been widely use to treat (stabilisation/solidification process) or reuse (into concrete or road materials) waste materials. In theory, cementitious materials can significantly reduce the release of toxic species by providing an environment of high alkalinity, which buffers against the types of acid attack experienced in the field conditions. In practice, however, there are complex interactions between waste components and binders that can lead to both short (delaying or poisoning of the normal hydration reaction) and longer (release of heavy metals in groundwater) term difficulties.

For the purpose of this study we have selected 3 different foundry waste materials that have been collected from various plants in the UK. It is important to note that very little is known about the environmental, physical and chemical behaviour of these solidified waste systems in view of beneficial reuse. Therefore, the objective of this paper is to investigate the effects of the major metal contaminants, Pb, Zn and Mn, on the mechanical, microstructural and leaching characteristics of the solidified waste materials.

2. MATERIALS AND METHODS

Three residues from foundry industry, provided by three companies, were studied. The first two, referred as waste 1B and 5B, are dusts extracted from above iron melting furnace powered respectively by electricity and coal. The third waste, referred as waste 10A, is a dust extracted from above a steel foundry.

The wastes were characterised physically and chemically. The elemental composition was determined by acid digestion and inductively coupled plasma (ICP) analysis, the oxide composition was determined by X-ray fluorescence (XRF). The mineralogical composition was investigated by X-ray diffractometry (XRD). The water content was measured using ASTM D2216 (1980) and the loss on ignition (LOI) was determined using ASTM C25. In order to predict the amount of water absorbed by the wastes, the water absorption capacity (WAC) of the wastes was measured. Thus, the wastes were soaked into demineralised water for 48 hours and then dried until constant mass at 110°C after filtration. The pozzolanicity of the waste products, defined as the capacity to react with calcium hydroxide to form compounds possessing cementitious properties, was also determined by using the standard EN 196 (1987) in an attempt to evaluate its effect on the final characteristics of the solidified product.

The solidified products were prepared at different water/cement and waste/cement ratios. Demineralised water was used as sole source of water and OPC was used throughout the experiments. Waste containing materials and controls were prepared following the ASTM C 305 method (1982). For wastes containing materials, the wastes, finely ground down to 150 μm, were previously mixed with OPC. Samples for UCS test were moulded in 50*50*50 mm moulds, vibrated for 15 s and stored at 100% relative humidity. After 1 day, the samples were removed from the moulds and stored at 100% relative humidity in sealed boxes (no carbonation, as checked with phenolphthalein, occurred before UCS test). Samples for other experiments were moulded in plastic moulds and vibrated for 15 s. Moulds were sealed until the experiments were conducted.

After 56 days of curing, physical and chemical characterisation of the solidified products was conducted. Elemental composition, oxide composition and mineralogical composition were determined using the same techniques as for the raw wastes. Bulk density and moisture content were also measured. Moisture content was determined by drying the sample at 60°C until constant mass. Mechanical, microstructural and leaching characteristics of all the samples were investigated as indicators of the quality of the cement hydration, main criterion of durability.

- Setting time was determined according to ASTM C191-82 (1982) using the formulations shown in Table 2 rather than the standard consistency.
- Unconfined Compressive Strength was measured in triplicates at 1, 7, 28, 56 days according to ASTM C109-87 (1987).
- Mineralogical composition was examined by X-ray diffractometry after 56 days of curing using a Philips 2000 System diffractometer employing copper k-alpha radiation at a scanning speed of 1° 2-theta/min.

- Acid Neutralisation Capacity (ANC) test was conducted after 56 days of curing, according to the method developed at Environment Canada's Wastewater Technology Center (Stegemann and Cote, 1991). This protocol provides an acid buffering capacity. Thus, eleven aliquots of finely crushed material (< 150 μm) are contacted with nitric acid solutions of varying concentrations to cover a range of pH from 1 to 13. The liquid/solid (L/S) ratio was 6 ml/g dry sample. After a contact time of 48 hours under agitation, the leachates are filtrated through 0.45 μm pore size polypropylene membranes and the leachate pH of each extract is measured.

3. RESULTS AND DISCUSSION

3.1. Physical and chemical characterisation of the waste materials

Physical and chemical characterisations of the wastes are presented in Table 1. The wastes presented very different water absorption capacity, ranging from 13% for waste 5B to 44% for waste 1B. This result was considered when preparing the solidified products. None of the wastes satisfied the pozzolanicity test. The XRD analysis of the wastes showed that the main crystalline components of waste 1B is calcite. Waste 10A is mainly composed of magnetite while waste 5B in addition to quartz and magnetite contains a large amount of amorphous material. Although the wastes are by-products from the same industry, they all presented significantly different chemical characteristics.

Table 1: Physical and chemical characterisation of the wastes.

	Elemental composition of the wastes, [mg/kg]						
Waste	**Al**	**Ca**	**Cd**	**Cu**	**Fe**	**K**	**Mg**
1B	644	282123	11.24	19994	19994	433	839
5B	4380	8954	n.d.	103	179751	1486	1219
10A	3743	76570	72.75	530	217087	13715	77692
	Mn	**K**	**Na**	**Ni**	**Pb**	**Zn**	
1B	6670	433	460	15.3	1578	27352	
5B	8292	1486	821	442	1650	5334	
10A	54164	13715	5562	225	1106	8000	

	Oxide composition of the wastes, [%]					
Waste	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MnO**	**MgO**
1B	69.36	6.9	1.93	9.76	0.97	0.72
5B	1.69	42.42	3.41	35.37	1.16	0.62
10A	13.89	3.63	1.51	44.2	6.67	13.89

Waste	**Water content, %**	**LOI, %**	**WAC, %**
1B	0.79	37.4	44
5B	0	22.89	13
10A	0.63	-0.32	28

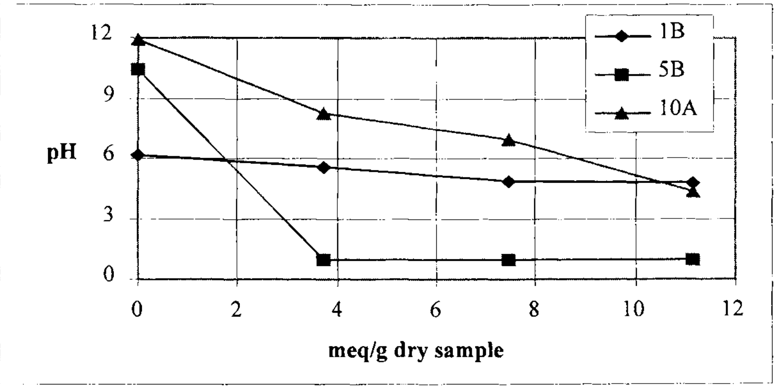

Figure 1: Acid neutralisation capacity of raw wastes

Results obtained from the ANC tests, presented in Figure 1, revealed that all three wastes had different buffering capacity behaviour. Waste 1B had a relatively low natural pH of 6 but presented a steady behaviour with a relatively small slope to pH 4.7 achieved after addition of about 11 meq/g of dry sample. This behaviour is due to its high calcite content. The buffering capacity of the waste 5B was small ; less than 4 meq/g of dry solid was needed to achieve pH 1. This result indicates the presence of significant amounts of inert material in accordance with the XRD results. However, waste 10A had a high natural pH of about 12 and a relatively high buffering capacity. About 11 meq of acid/g of dry sample was required to achieve a pH of around 4.

3.2. Solidified products formulations

For each waste, mixtures at different waste/cement ratio (0.01, 0.05 and 0.1), were prepared. As suggested by the wastes' WAC (water absorption capacity), two water/cement ratios (0.4 and 0.45) were selected. Furthermore, two controls were prepared under the same water/cement ratio conditions. Details of the different mixture formulations are presented in Table 2.

Table 2: Formulation of the mixtures [% total weight], water/cement and waste/cement ratios

	Product	Cement	Water	Waste	Water/Cement	Waste/Cement
Control	Control 1	71.4	28.6	-	0.4	-
	Control 2	69	31	-	**0.45**	-
Waste 1B	1B1	70.9	28.4	0.7	0.4	0.01
	1B5	69	27.6	3.4	0.4	0.05
	1B10	34.5	29	6.5	**0.45**	0.1
Waste 5B	5B1	70.9	28.4	0.7	0.4	0.01
	5B5	69	27.6	3.4	0.4	0.05
	5B10	66.7	26.7	6.6	0.4	0.1
Waste 10A	10A1	70.9	28.4	0.7	0.4	0.01
	10A5	69	27.6	3.4	0.4	0.05
	10A10	34.5	29	6.5	**0.45**	0.1

3.3. Effect of waste addition on setting time

Initial and final setting time of each product are presented in Table 3. Figure 2 illustrates the setting time of the waste containing materials compared to Control 1 (W/C=0.4), except for the mixtures containing 10% of waste 1B and 10A which are compared to Control 2 (W/C=0.45).

The results showed that addition of waste 1B and waste 10A had an increased effect on the setting time depending on the waste/cement ratio. Increased levels of wastes induced a retardation of the setting times. The effect is more pronounced for waste 1B as the setting time at 10% addition (1B10) was retarded by 250% compared to Control 2. This result could be due to the presence of high levels of Zn (Table 1), which has been reported in the literature to be a retardant (Arliguie, 1982, Poon, 1985). On the other hand, addition of waste 5B didn't have much effect on both initial and final setting times. For the lower waste/cement ratios of 0.01 and 0.05, setting times were slightly reduced compared to Control 1.

Table 3: Initial and final setting time of the products

Time, min	**Control 1**	**1B1**	**1B5**	**5B1**	**5B5**	**5B10**	**10A1**	**10A5**
Initial setting	260	260	470	245	265	280	350	490
Final setting	360	360	670	330	350	390	440	600

	Control 2	**1B10**	**10A10**
Initial setting	310	1140	600
Final setting	420	1500	695

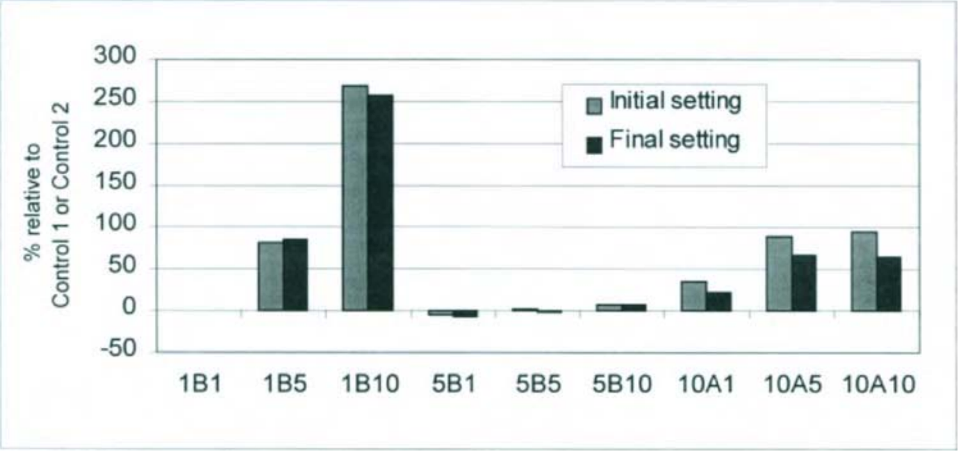

Figure 2: Initial and final setting times in percentage relative to Control 1 or Control 2

3.4. Effect of waste addition on UCS

Comparisons, at equal water/cement ratio, of the UCS of the wastes containing materials and Controls are presented in Figure 3.

Compared to Control 1, addition of 1% and 5% of waste 1B reduced the UCS at 1 day but slightly increased it at 7, 28, 56 days. Indeed, setting time was delayed for the waste products 1B1 and 1B5 compared to Control 1 (Table 3). Compared to Control 2, addition of 10% of waste 1B significantly reduced UCS at 1 day by 76% which is expected due to the important delay in its setting time (Table 3). However, after 7 days of curing, the UCS of the 1B10 product is about 30% higher than the UCS of the Control 2 but for 28 and 56 days the difference between the two products decreased.

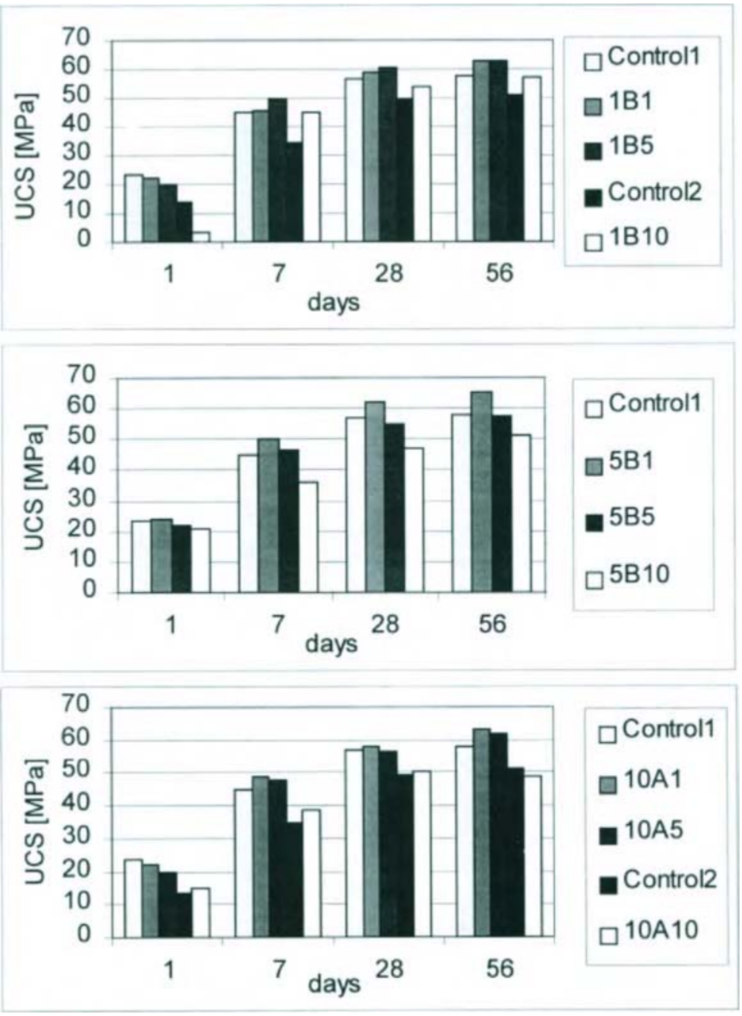

Figure 3: Effect of waste addition on UCS

Compared with Control 1, 1% and 5% of waste 5B addition had little effect on the strength of the final product, however, a 10% addition reduced the UCS by up to 20%. At equal water/cement ratio, addition of waste 10A had negligible effect on the UCS.
Overall, the results revealed that after 28 days the UCS of most waste products is within ±10% of the controls (water/cement = 0.4 and 0.45).

3.5. Effects of waste addition on mineralogical composition investigated by XRD

XRD analysis results of three products after 56 days of curing time are presented in Figure 4.

Considering the complexity of the products, interpretation of the data was only qualitative. The results showed that the higher the waste/cement ratio was, the more ettringite peaks intensity was reduced and the more non-hydrated products (i.e., C_3S and C_2S) were detected. At 5% of waste 1B, calcite, which was originally present in the raw waste, was detected.

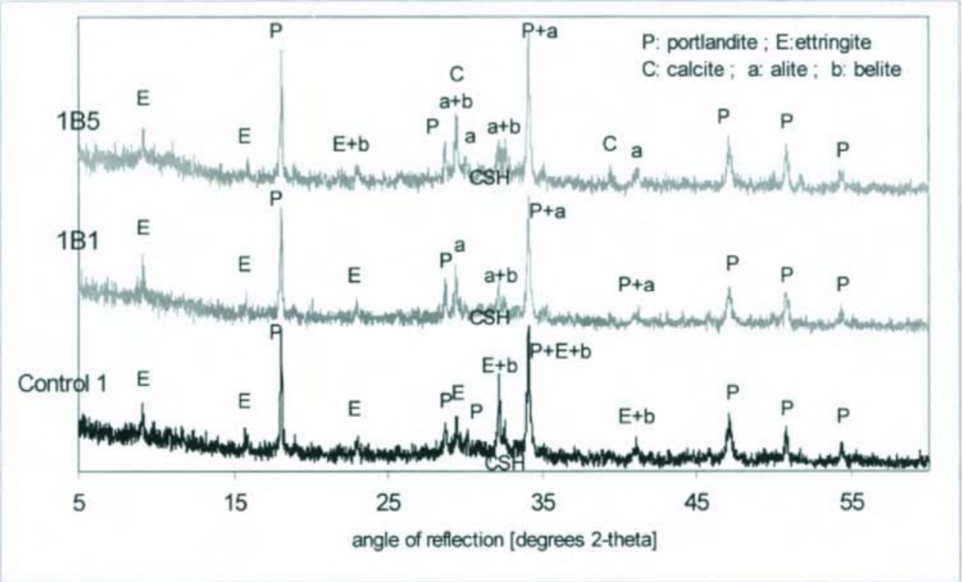

Figure 4: Effects of waste addition on mineralogical composition (XRD).

3.6. Effect of waste addition on ANC (acid neutralisation capacity)

ANC curves of the solidified products are presented in Figure 5. Comparison of the ANC of Control 1 and Control 2 showed that the water/cement ratio had no perceptible effect on the buffering capacity of the materials. Considering this result, ANC of all wastes containing materials were presented in comparison to Control 1. Compared to the ANC of the non-treated wastes, as shown in Figure 1, it is clear that the addition of cement provided a considerable buffering capacity due to the production of calcium hydroxide during the cement hydration. Based on the acid quantity required to reach pH 11.9, the amount of calcium hydroxide, produced during the hydration reactions of the cement, was estimated at 148g/kg of dry material and is approximately the same for all the materials. The pH titration curves for all the materials exhibited a continuous decrease from pH 12.5 to pH 10 achieved for 14 meq/g of dry material followed by a drop to pH 2 achieved after addition of 20 meq/g of dry material.

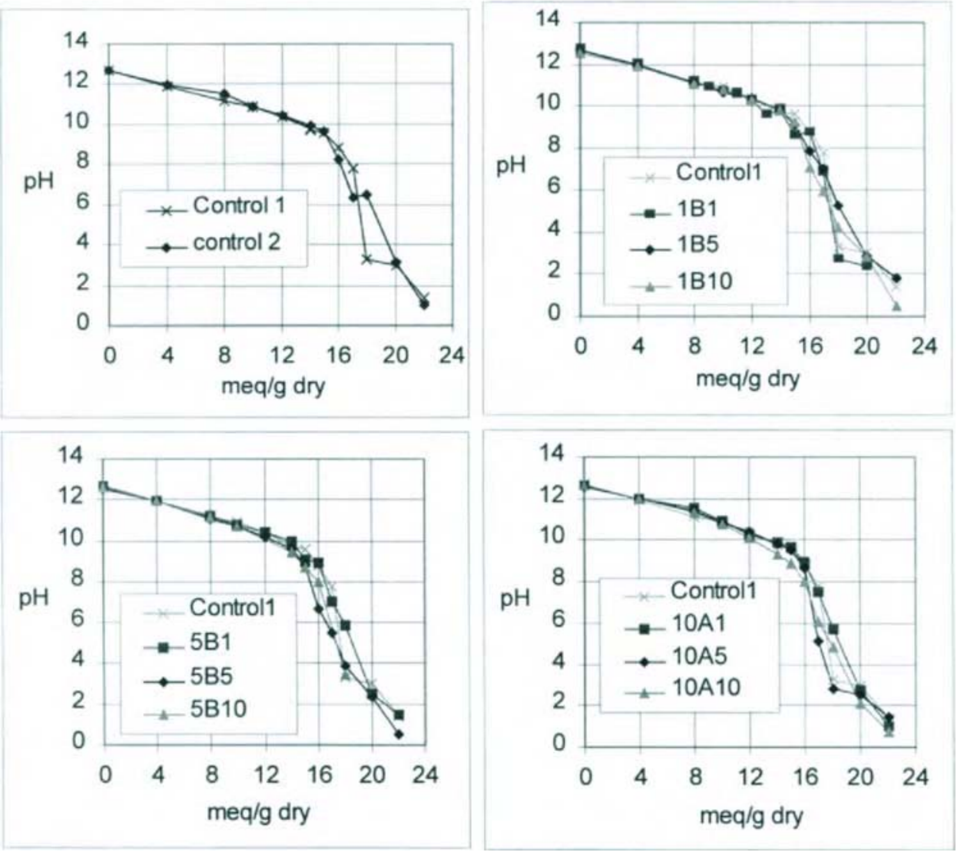

Figure 5: Acid neutralisation capacity of all the materials.

Overall, the results showed that the buffering capacity of the solidified products is not perceptibly affected by the type, neither the waste/cement ratio for pH higher than 10. Very slight differences seemed to appear in the drop zone. These results are very interesting from the point of view that the introduction of wastes to cement did not affect the buffering capacity of the final products.

4. CONCLUSIONS

- Addition of wastes with high content of zinc (1B and 10A) caused a significant retardation in the setting time.
- After 28 days, the UCS of most waste products is within +10% of the controls.
- Addition of wastes suppressed the level of hydration (non-hydrated products are detected) as shown by the XRD spectra.
- Addition of waste had no effect on the buffering capacity for pH higher than 10. It was for waste/cement ratio higher than 0.05 that the effect on ANC was detectable for pH lower than 10.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Physical Properties and Acid Neutralisation Capacity of Incinerator Bottom Ash - Portland Cement Mixtures

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The amount of bottom ash resulting from solid waste incineration typically ranges from 30 to 35% of burnt waste. Although such a residue stream is not classified as a hazardous waste according to the European waste catalogue, disposal of bottom ash may heavily weigh on the overall incineration costs.

Furthermore, the present tendency for solid waste management in industrialised countries is towards reduction of the amount of wastes to be landfilled.

With a view to that, technical approaches aimed at reusing residual streams in industrial applications as secondary materials must be strongly encouraged.

As far as bottom ash is concerned, a promising option is represented by blended cement formulation. Bottom ash is indeed characterised by the presence of oxides and alumino-silicates, which might be responsible for strength development during cement hydration. In some cases, depending both on the composition of the original waste and on the combustion technology adopted, bottom ash may also exhibit pozzolanic activity.

It is well known that the properties of hardened cement mixtures made with impurities-bearing materials are strongly affected by the physical-chemical characteristics of the components, as well as the waste/cement dosage.

This paper presents the results of an experimental investigation on the behaviour of mixtures made with Portland cement and bottom ash coming from an Italian medical waste incinerator. In particular, the influence of waste/binder replacement levels and water/solids ratios on strength development and acid neutralisation capacity was investigated.

Different samples were prepared at low and high waste/binder ratios at various amounts of added water in each mixture. Physical properties consisting of setting time, unconfined compressive strength and evaporable water content were measured at different ages.

Also, the acid neutralisation capacity of the hardened material was evaluated in order to investigate the leaching behaviour under different pH conditions.

In order to quantify to what extent do the above parameters affect the properties of the solidified products, a factorial design was arranged and the analysis of variance carried out.

1. INTRODUCTION

The amount of bottom ash, including grate siftings, resulting from waste incineration, typically ranges from 30 to 35 % of burnt waste by weight.

While great concern has been addressed so far in order to assess the feasibility of treating the APC residues in view of reuse or disposal, much less information concerning bottom ash is available in the literature.

Nonetheless, the amount of bottom ash generated represents the major portion of the solid residues resulting from waste combustion. Consequently, bottom ashes, although classified as non-hazardous materials according to the European Waste Catalogue, actually require high expenditures to be disposed of.

In light of the above considerations, technical approaches aimed at reusing incineration bottom ashes as secondary materials must be strongly encouraged. This may result in two main beneficial effects: *1)* reduction of the amount of residues to be landfilled, *2)* partial substitution of raw materials in industrial applications. Among the various applications proposed for bottom ash, a number of studies are available on use of bottom ash either in road construction [1] or as an aggregate in concrete. In some cases, it was recognised that the high chemical reactivity exhibited by bottom ash could cause some long-term detrimental effects on the properties of the final product [2]. On the other hand, advantage may be taken from the presence of reactive compounds, such as oxides and alumino-silicates, in bottom ash with a view to the formulation of blended cement. It should also be stressed that in some cases, depending on the composition of the original waste and on the combustion technology adopted, bottom ash may also exhibit pozzolanic activity as a consequence of high contents of amorphous, highly reactive silica.

2. INCINERATOR BOTTOM ASH COMPOSITION

Studies conducted to investigate bottom ash mineralogy [3] revealed that, as expected, incineration bottom ash is predominantly composed of high-temperature solids, referred to as primary phases, most of which are metastable under natural conditions and are, therefore, likely to undergo chemical modifications leading to thermodynamically stable assemblages or minerals, often called secondary phases [4].

Clozel et al. [3] showed that, apart from the presence of unburned material, fresh incinerator bottom ash is generally composed of a low-density, impurity-bearing slag phase and a vitreous phase with variable quantities of crystals and glassy material. The most common phases were recognised to be silicates (quartz), alumino-silicates of Ca and Na (plagioclase, ghelenite, piroxene, olivine, alite, belite), metal oxides, hydroxides (portlandite), sulphates (anhydrite), carbonates (calcite, siderite), as well as metals and alloys [3], [5].

The high reactivity of the above mentioned primary phases during bottom ash aging leads to the formation of secondary phases, including both new phases such as gypsum and ettringite, and neoformed carbonates, sulphates, oxalates, hydroxides and zeolites, as well as amorphous species.

Carbonate precipitation is the result of portlandite stabilisation due to the uptake of atmospheric CO_2. This phenomenon is also responsible for some metals entrapment, by means of either encapsulation into the calcite lattice or precipitation in the form of chromates, phosphates and sulphates [3].

While the occurrence of portlandite carbonation represents a fixation mechanism for some heavy metals, the presence of portlandite may also be responsible for the formation of aluminium hydroxides and complex calcium silico-aluminates, that exert swelling and cracking effects when bottom ash is to be reused in concrete [1], [6].

3. MATERIALS AND METHODS

3.1. Materials

The experimental work was carried out on a bottom ash coming from an Italian medical waste incinerator. The laboratory programme followed a wider protocol adopted by the NNAPICS consortium [7], making use of both standard procedures and internal methods as summarised in Table 1. The results of the analytical determinations are shown in Table 2 in terms of mean values of three replicates.

A class 42.5N Portland cement was used as the solidifying agent.

3.2. Testing methods

The mixtures were prepared at varying waste/cement and water/total solids ratios. In particular, the waste content of the mixtures was varied over the range 10 - 80% of total dry solids (10%, 20%, 30%, 50% and 80%), whilst the selected water/solids ratios were 0.30, 0.35 and 0.40. Distilled water was used as mixing water. Furthermore, control samples were prepared at 0% waste addition at the same water/solids ratio values.

Table 1

Summary of methods

Raw waste		Treated waste	
Property	Method	Property	Method
Sample preservation	ISO 5667	Mixing	ASTM C305
Homogenisation	Quartering (IRSA-CNR)	Particle size reduction	Ball milling (□<150 □m; in inert environment)
Particle size reduction	Ball milling (□<150 □m)		
Digestion	APHA 3030H	Moisture content	ASTM D2216 (60°C)
	IRSA-CNR (Hg)	Bulk density	Measurement of volume and weight
	IRSA-CNR (As, Sb)		
Sulfates	UNI 8520	Time of Setting	ASTM C191
Chlorides	UNI 8520	Unconfined Compressive Strength	ASTM C109 at 1, 3, 7, 28, 56 days
LOI	ASTM C25		
Moisture content	ASTM D2216	Acid Neutralisation Capacity	ANC-WTC method
Bulk density	ASTM C29		
Acid Neutralisation Capacity	ANC-WTC method		

Table 2

Physical - chemical characterisation of the bottom ash (mg/kg)

Element	Concentration	Element	Concentration
Al	8391.8	Pb	196.5
Ca	22985.3	Zn	201.2
Cd	n.d.	As	4.2
Cr	168.1	Hg	0.05
Cu	1084.1	Sb	2.44
Fe	4658.6	Chlorides	n.d.
K	3263.6	Sulphates	1400
Mg	3176.7	L.O.I. (%)	5.56
Mn	71.5	Water Content (%)	13.65
Ni	332.2		

n.d.: not detectable

The specimens were cast in 50x50x50 mm moulds and cured at room temperature under R.H. conditions >95% for different times. Selection of the sample preparation schedule was made according to a randomised sequence, so as to prevent the effects of unknown nuisance variables, perhaps varying out of control during the experiments, from contaminating the results.

Mixtures and specimens were tested for setting times and unconfined compressive strength at different ages (1, 3, 7, 28, and 56 days), as well as for evaporable water content and acid neutralisation capacity (ANC) at a 56-day age. UCS and evaporable water content measures were taken in triplicate. For high waste contents (50 and 80%), no testing at 1 and 3 days was carried out because setting was strongly delayed.

The adopted procedures are shown in Table 1.

3.3. Statistical procedures

A two-way replicated factorial design [8], [9] for each of the above mentioned response variables was analysed by means of a two-way analysis of variance (ANOVA). The results to be shown correspond to separate analyses for each measure, namely unconfined compressive strength, evaporable water content and setting time. The independence between the two response variables was assumed through the analysis, so that univariate linear models were fitted.

The analysis was aimed at inspecting the effect of waste dosage and water content on the evolution of hydration and on the final properties of the solidified mixtures. For each curing time, the experimental data for each variable of interest were arranged in a two-way table, its rows representing the first of the factors controlled for, namely % dry weight of waste in the mixture, and its columns standing for the second experimental factor (i.e., % weight water on total dry solids).

Since replicates for each combination of factors were available, estimation and testing of interaction effects was carried out.

The main characteristic of a two-way factorial design is that both factors, each of them representing a treatment, are of equal interest (none of them representing a block variable), and moreover the two treatments may exhibit *interaction*. This would mean that one treatment may affect the other, so that taking combinations of the factor levels may yield responses which are different from what might be assessed marginally: that is, even though factor 1 shows, say, a positive effect on the response, in combination with a particular level of factor 2 it may yield a negative mean response, thus making the former treatment level ineffective, while leaving the latter unchanged.

In a two-way factorial design the aim is at estimating and testing the marginal effects of each factor (*main effects*), as well as their joint effect (*interaction*), if any. In the latter case, the model to be fitted will no longer be *additive*, as the data could more conveniently be represented by the linear model

$$Y_{ijk} = \mu + \alpha_i + \beta_j + \gamma_{ij} + \varepsilon_{ijk} \qquad \text{(a)}$$

in which the combined effect of the two treatment levels i,j is represented by be the sum $\alpha_i + \beta_j + \gamma_{ij}$. This is easily seen to result in a model where it will no longer be possible to *separate* the treatment effects.

On the other hand, the above mentioned additive model is written as

$$Y_{ijk} = \mu + \alpha_i + \beta_j + \varepsilon_{ijk} \qquad \text{(b)}$$

Choosing between (a) and (b) will be one of the crucial points of the analysis, since when looking for a model, e.g. a synthetic representation of the data, the aim is at finding the one which provides an accurate description of the observables, at the same time retaining simplicity and ease of interpretation.

In each of the formulas above, the indexes $i=1,...,I$, $j=1,...,J$ are associated with the treatment levels (in our case, I = number of % waste levels, J = number of % water levels selected), while k stands for the replications ($k = 1,...,K$). μ represents the overall mean, while α_i and β_j are the (incremental w.r.t. μ) effects of the "% waste" and "% water" treatments; finally, the γ_{ij}'s are the above mentioned interaction effects.

In both models the ε_{ijk}'s are the error terms, assumed to be mean zero normal and homoschedastic. These represent the major assumptions of the model. Hence, inferences and conclusions based on such models are only valid conditional on the previous assumptions being met, which motivates use of diagnostic tools, commonly based on residuals.

In case of no interaction as stated in model (b), the treatments act additively, so that every expected cell response (which, supposedly, is affected by the particular combination of treatment levels used) can be represented as $\mu_{ij}=E(Y_{ijk})= \mu + \alpha_i + \beta_j$; if however model (a) holds, an extra-term is needed, namely the interaction effects γ_{ij}, so that the expected response will now be written as $\mu_{ij} = \mu + \alpha_i + \beta_j + \gamma_{ij}$, the latter term in the equation representing the incremental effect due to the combination of the i-th "%waste" and j-th "%water" treatment levels.

Statistical theory gives us a simple procedure for estimating each parameter in the model according to the following data breakdown which corresponds to the regression model above:

$$\bar{y}_{ij} = \bar{y} + (\bar{y}_i - \bar{y}) + (\bar{y}_j - \bar{y}) + (\bar{y}_{ij} - \bar{y}_i - \bar{y}_j + \bar{y}) \qquad (1)$$

The magnitude and signs of the estimated coefficients also give indication of the relative importance of the treatment (interaction) levels.

ANOVA, which is a standard formal statistical procedure, was used to assess statistical significance of the main and interaction effects of the treatments, so as to formally evaluate whether or not the factor levels affected the mean response.

In an ANOVA table, the total sum of squares (representing the overall variability) is decomposed into additive components, each corresponding to a different source of variation ("% waste", "% water" and "% waste-by-% water interaction"), plus the "residual" sum of squares (otherwise called unexplained variation). Each mean square term (sum of squares divided by the associated degrees of freedom), attributable to a specific source of variation, is then compared with the mean square error (residual sum of squares divided by the associated degrees of freedom). Under the previously mentioned assumptions and under the null hypothesis of no effects, each of the ratios is distributed according to an F-distribution, whose degrees of freedom are associated with each of the corresponding sum of squares in the ratio. A one-sided F-test on the ratio can thus be conducted. This corresponds to independent statistical tests on the model coefficients of the following form:

H_0: $\alpha_1 = \ldots = \alpha_I = 0$	H_0: $\beta_1 = \ldots = \beta_J = 0$	H_0: $\gamma_{11} = \ldots = \gamma_{IJ} = 0$
H_1:at least 1 coefficient $\neq 0$	H_1:at least 1 coefficient $\neq 0$	H_1:at least 1 coefficient $\neq 0$

An overall test for assessing the global fit of the model may also be constructed in a similar manner.

Several diagnostic tools based on the residuals were used in the present investigation, including normal quantiles plot and histogram of residuals for assessing normality, scatter plot of residuals versus predicted values for detecting non linearity and/or heteroschedasticity, which would possibly suggest transformation of the original data.

4. RESULTS AND DISCUSSION

Investigation of water and waste dosage on UCS will be discussed in the following.

Prior to the moment of estimation of main and interaction effects, an exploratory analysis was carried out, aimed at capturing the most relevant results and at detecting possible departures from the model hypotheses. For example, Figure 1 a) allows for a visual evaluation of the main effects, showing a clear trend of mean response with increasing levels of each treatment. This was confirmed by inspection of the box plots for each factor, which both showed considerable differences between the mean responses at different waste and water contents, so that an effect of each single treatment was expected.

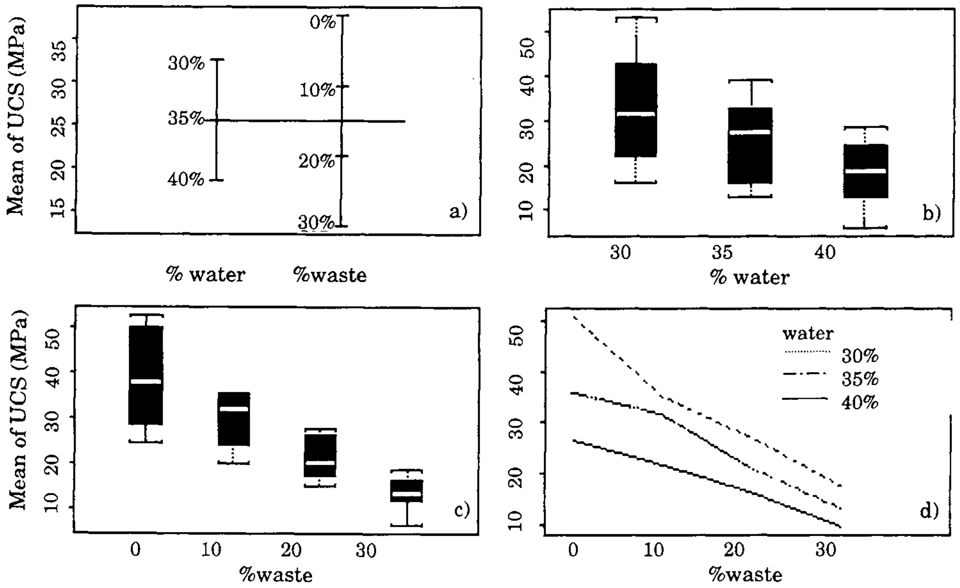

Figure 1. Exploratory data analysis for UCS (1-day curing)

A look at Figure 1 b) also revealed that interaction is not a deal in the case under analysis, so that an additive model is likely to be an appropriate representation of the experimental results. Examination of Figure 1c) and d) reassured about the assumption of homoschedasticity of the UCS values. The results of the UCS determinations for 1 day curing are represented in Table 3 in terms of the overall mean and the treatment effects. For each curing time, the models were always found to be highly significant, as shown by the ANOVA tables. As an example, in Table 4 the ANOVA table for the UCS values at 1-day curing is shown.

Note that for each curing time, inspection of the ANOVA table lead to adoption of model (b). In the case under analysis, figure 1 d) gives in fact a first, visual indication of absence of interaction effects; this was confirmed by inspection of the ANOVA table for model (a), which shows non-significant interaction effects, the latter conclusion being supported by low p-values.

When additivity holds, the combined effect of the two factors taken together can simply be derived by addition of the main effects related to the corresponding level of the factors.

Secondly, model checking was carried out after the estimation phase. Figure 2 presents the results obtained for samples characterised by an age of 1 day.

By inspection of the histogram and the so-called q-q plot of residuals, the hypothesis of normality was judged, a symmetric histogram and a linear q-q plot being indication of gaussian error distribution.

Table 3
Factors effects on UCS at 1-day curing

Curing time (d)	% water (□$_i$)			% waste (□$_i$)						Overall mean (MPa)
	30	35	40	0	10	20	30	50	80	
1	+7.1	-0.1	-7.0	+12.2	+4.0	-4.0	-12.2	----	-----	25.6
3	+8.9	-0.5	-8.4	+16.5	+4.4	-6.4	-14.5	----	----	37.4
7	+7.1	-0.3	-6.8	+31.5	+14.2	+4.3	-4.9	-18.3	-26.9	30.4
28	+8.2	-1.2	-7.1	+26.4	+17.3	+7.2	-6.7	-17.4	-26.7	35.4
56	+8.1	-0.4	-7.7	+29.1	+24.2	+2.0	-5.4	-19.3	-30.5	41.0

Table 4
ANOVA table (UCS, curing time = 1 day)

Source of variation	d.f.	□ squares	Mean squares	F Value	Pr(F)
% water	2	1194.7	597.4	48.0	4.5 e-10
% waste	3	2967.8	989.2	79.5	2.2 e-14
Residuals	30	373.3	12.4		

Finally, the scatter plot of residuals versus fit (not shown here) did not exhibit any clear relationship, which would be interpreted as model inappropriateness. The results obtained and discussed so far do not seem to suggest any severe deviation from the model hypotheses. Thus, it can be stated that, when considering the hardening process, the combination of the two factors results in no additional effect with respect to the one associated with the individual factors (i.e., the marginal effect).

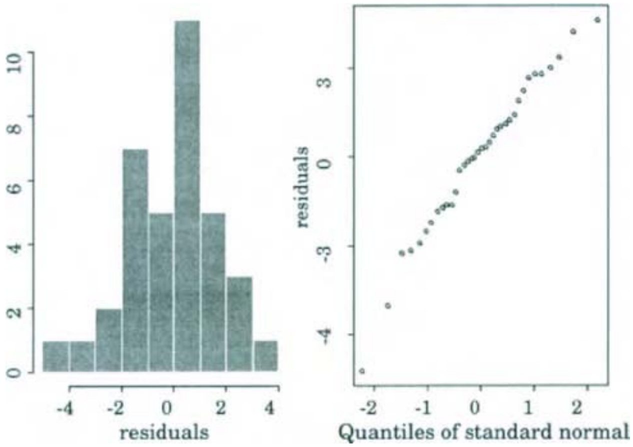

Figure 2. Check for normality for the UCS measurements

From Figure 1 linearity of the effects can also be observed, thus implying that increasing the waste dosage or the water content of the mixtures results in an approximately proportional decrease in strength at all the examined curing times. This behaviour was also confirmed by the values of the evaporable water content at 56 days.

Under such conditions, the bottom ash used in this study can be regarded to as exerting only a dilution effect with respect to Portland cement, without exhibiting any poisoning action on the solidified matrix. Evidence of this behaviour is also provided by the shape of the curves showing the decrease in mechanical strength as a function of the water/cement ratio of the samples (as calculated based on the waste and water content of each mixture), depicted in Figure 3. The UCS measurements at each curing time were fitted by the following model:

$$\mathrm{UCS} = \frac{a}{\left(\frac{\mathrm{W}}{\mathrm{PC}}\right)^{b}} \tag{2}$$

(where W/PC represents the water/cement ratio and a and b are two constants), that is commonly accepted for hydrated Portland cement [10]. Interpolation of the observed data showed b values ranging from 1.8 to 2.4, close to the value $b = 2$ generally observed for cement.

This consideration suggests the opportunity to carry out further investigation aimed at either testing appropriate activators in order to improve the strength development of the bottom ash, thus minimising its dilution effect, or using such a material as an aggregate in concrete formulation.

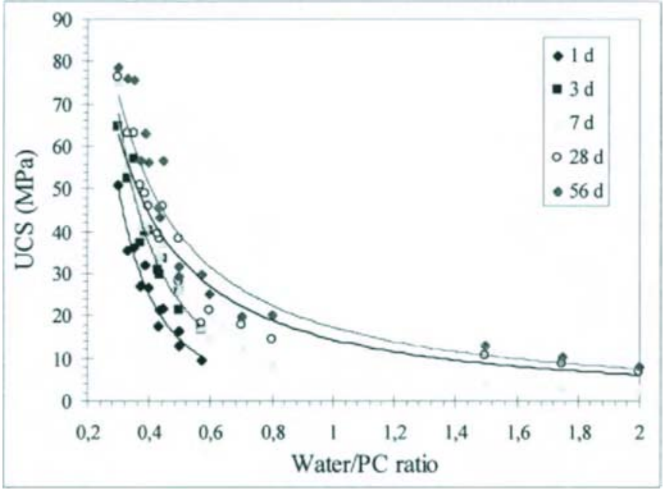

Figure 3. UCS as a function of the water/cement ratio

As far as the results of initial and final setting times determination were concerned, it is to be stressed that the hypotheses of the model were not met, as suggested by the above mentioned model checking procedures. In particular, a strong relationship between the residuals and the fitted values was clearly revealed. The variability of the residuals increased with increasing fitted values. As a consequence of this, a variance-stabilising transformation was thought to be necessary in order to make variance equal across the treatment levels. It was based on evaluation of the regression line obtained by plotting the absolute residuals versus fitted values on a logarithmic scale. From that analysis a square root transformation was shown to be appropriate for variance stabilisation of setting time values. In any case, the presence of some outliers was evidenced even after such a transformation, corresponding to the samples with an 80% waste content at 35 and 40% water contents. In the absence of replicates, it is not possible to conclude if it may have been caused by random errors during the test, such as the lower ambient temperature at which those measurements were carried out, or is an indication of a change in setting behaviour with high waste contents. Work is in progress in order to verify or reject this tempting hypothesis.

Anyway, it is worth stressing that what was observed for setting times does not have any big practical implication, the values for them lying for all the examined mixtures within technological limits (approximately 45 minutes for the initial value and 12 hours for the final one).

From the analysis performed, also non-linear, more than proportional, effects exerted by the two factors on setting times were observed.

The ANC test was performed in order both to assess the capability of the solidified material to resist acidification and to investigate on the formation of hydration products. Evaluation of the acid neutralisation capacity of a solidified material is a valid tool to determine the possibility to maintain alkaline conditions within the solid matrix, under which contaminants have low solubilities and dissolution of the matrix is prevented [11].

On the other hand, the results from the ANC test can successfully provide indications about the presence and relative amount of hydration products within the solidified matrix.

Starting from the fact that the analysis of strength evolution did not reveal any effect of the two factors other than a mere dilution, no statistical investigation was carried out for the ANC test. Instead, differential acid neutralisation analysis according to the method proposed by Glass and Buenfeld [12] was performed for the samples with a waste dosage of 10, 20, 30 and 50% at water contents of 30, 35 and 40%.

The results of the ANC test are presented in terms of final pH after 48-hour extraction as a function of the amount of nitric acid added to the sample. The presence of intervals where a resistance to a fall in pH occurred was evidenced by the cotangent of the titration curve plotted versus the amount of acid added. The results are depicted in Figure 4 for the mixtures with a waste dosage of 10 and 20% at a water content of 35%.

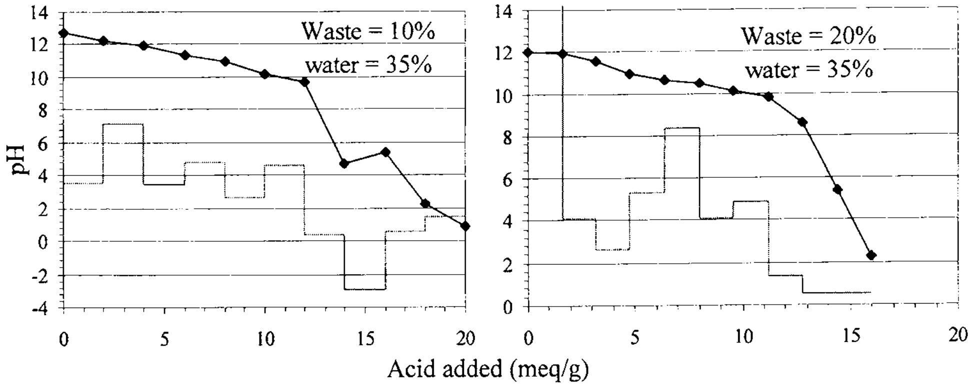

Figure 4. Titration curve and differential ANC analysis

For the other examined mix formulations a similar analysis was carried out, the results being summarised in Table 5 in terms of pH values observed for the various significant plateaus. According to what was shown by different researchers [11], [13], it is tempting to hypothesise that the first peak (pH ≈ 12) is due to the presence of highly soluble portlandite, while the second peak (pH ≈ 11.2) could be ascribed to CSH and/or ettringite phases. Microstructural investigation is on the way in order to assess the validity of such hypotheses. The change in pH plateau values from sample to sample could be attributed either to the variation of the Ca/(active)Si ratio with increasing the waste dosage, or to the change in the hydration phases nature in the presence of contaminants.

5. CONCLUSIONS

The influence of waste dosage and water content on the properties of solidified incinerator bottom ash - Portland cement mixtures was investigated through a two-way replicated factorial design.

Table 5
pH values at each plateau

Waste dosage (%)	Water content (%)	pH plateau 1	pH plateau 2	pH plateau 3
10 %	30	12.8	11.40	Not recognised
	35	12.07	11.14	9.96
	40	12.63	11.22	Not recognised
20 %	30	12.80	11.30	Not recognised
	35	12.00	10.60	9.95
	40	11.20	10.74	Not recognised
30 %	30	13.60	11.44	Not recognised
	35	Not recognised	Not recognised	Not recognised
	40	Not recognised	10.84	Not recognised
50 %	30	Not recognised	11.00	Not recognised
	35	Not recognised	11.80	Not recognised
	40	12.20	11.10	Not recognised

Different response variables including mechanical strength, evaporable water content and setting times were analysed.
The results showed that for unconfined compressive strength no interactions between the effects were recognisable. Moreover, linear dependence of strength from both waste dosage and water content was assessed. Conversely, for setting times a non-linear, more than proportional, dependence was observed.
Data derived from the ANC test analysis were used to infer on the presence of hydration phases within the solidified matrix. Further investigation is on the way in order to clarify about mineralogical aspects.
The information which resulted from the present experimental work seems to suggest that the examined bottom ash should be better reused as an aggregate in concrete rather than for blended cement formulation.

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Synthesis of Solidification Experience for Synthetic Wastes

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The NNAPICS project is being conducted to try to predict the effects of impurities in wastes on the final properties of cement/waste products using data mining techniques, such as neural network analysis, applied to data collected from the literature. The data collected by the project includes information for more than 500 solidified products prepared using synthetic wastes. As synthetic wastes are less complex than real wastes, interactions with contaminants should be easier to characterise in products prepared with synthetic wastes. Neural network models were constructed for portland cement systems containing barium, cadmium, chromium, copper, lead, nickel or zinc, as oxides, hydroxides, nitrates, or chlorides, from 8 literature sources. The models were able to predict unconfined compressive strength and pH with excellent correlation between measured and predicted values. The effect of the heavy metals on the Portland cement was more evident for pH, than for unconfined compressive strength.

1. INTRODUCTION

The properties of Portland cement are controlled by strict specification of its elemental and mineral composition. It is well known that addition of even small amounts of impurities can substantially alter the behaviour of this material, in ways that are difficult to predict. And yet, introduction of impurities into cement systems may be unavoidable when utilising industrial by-products in construction applications and when using cement to improve the chemical and physical properties of industrial wastes prior to disposal.

The academic and technical literature contains results from thousands of experimental case studies that have been conducted in order to try to predict the final properties of products made by mixing cements and wastes, and avoid the practical and environmental problems which may result from the interactions of waste with cement. Currently, most of these studies stand on their own, without clear relationship to the others. A project is being undertaken through the European Commission's Industrial and Materials Technologies Programme (BRITE-EURAM III) to try to synthesise the information in the literature by collecting the data and using neural network analysis to perform data mining to identify useful predictive relationships in it.

At the time of writing, the Neural Network Analysis for Prediction of Interactions in Cement/Waste Systems (NNAPICS) project has created a database in Microsoft Access containing more than 900 references from the literature and industrial sources. Data has been collected for nearly 8000 cement/waste products, involving more than 100 waste types (according to the European Waste Catalogue) from approximately 300 of these references. The six most common wastes are coal fly ash, incinerator fly ash, synthetic waste, baghouse dust, plating waste, and blast furnace slag. Fernandez et al. (2000) has prepared a more detailed analysis of the collected data.

The collected data includes all of the information concerning experiments conducted with synthetic wastes that could be found by the project team. As synthetic wastes are less complex than real wastes, interactions with contaminants should be more easily characterised in products prepared with synthetic wastes. Therefore, analysis of the data for these products has been prioritised, and is the subject of this paper.

2. METHODS

2.1. Data Pre-Processing

One of the main requirements of successful neural network analysis is a large data set which is representative of the domain of the problem. Thus, the first task in creating a neural network model was to screen the collected data to determine which variables of interest were found in the literature with sufficient frequency to allow a neural network to be trained. Queries and macros were applied to the Access database to refine the data set in an iterative process. Pre-processing of the resulting training data set was required to verify that the data was valid and to deal with missing values. Scale transformations and categorical variables were not a concern for the work reported here.

2.2. Neural Network Analysis

Function approximation, i.e., regression or classification, problems, such as prediction of the properties of cement/waste systems, are best addressed using feedforward networks, using either supervised learning in a multilayer perceptron architecture, or hybrid learning in a radial basis function network. In these neural networks, multivariate non-linear functions are modelled as composites of simpler non-linear activation functions (e.g., the sigmoid function) such that, in theory, any multidimensional surface can be approximated. A glossary of basic neural network concepts may be found in Stegemann and Buenfeld, 1999. The commercial software package Trajan Neural Network Simulator, Version 4 (Trajan, 1999) was used to create the neural network models for this paper. This software includes feature selection and pruning algorithms, to help select the most important variables, and identify an optimal network architecture. It can also analyse the sensitivity of the models created to the individual input variables.

3. RESULTS AND DISCUSSION

3.1. Data Pre-Processing

Examination of the data collected in the NNAPICS database showed that data were collected for 1830 products that contained synthetic wastes or pure compounds such as might be found in wastes. The original intent in studying the latter may have been unrelated to waste management, but both of these types of materials will be termed synthetic wastes for the purposes of this paper. The materials added to the cement system have been broken down into 6 categories, which are listed here from least to most complex:

1) Pure inorganic compounds and their mixtures. These salts may be added as accelerators or retarders in current practice in the concrete industry, and may also be found in many industrial wastes, including nuclear wastes.
2) Pure toxic metal compounds and their mixtures. Toxic metals are commonly found as contaminants in many industrial wastes, and are of concern because of their potential environmental impact, as well as their effect on cement hydration.
3) Pure organic compounds and their mixtures. Some of these organic compounds may be added as accelerators or retarders, and others are of environmental concern.
4) Mixtures of pure inorganic and organic compounds (including toxic metals).
5) Synthetic treated wastes. These include solutions of toxic metals that have been oxidised, reduced or precipitated.
6) Complex synthetic wastes. These include simulated specific waste types, such as slags, soils, etc.

Table 1 summarises the information collected for each category of material, in terms of the number of references that contain this data, the number of individual synthetic wastes represented, the number of cement/waste products prepared with the wastes, and the physical properties for which more than 100 measurements were collected (showing different replicates and curing times as separate entries). Collection of leaching data focussed on pH and contaminant concentrations from single batch extraction tests, such as the European DIN 38414 test (DIN, 1989) with distilled water, the USEPA Toxicity Characteristic Leaching Procedure (TCLP) (United States Environmental Protection Agency, 1999), the Dutch Availability Test NEN 7341 (NEN, 1995), and the Acid Neutralisation Capacity test (Stegemann and Côté, 1991).

Because of the heterogeneity of the data collected, it was necessary to further subdivide the data for the products containing synthetic wastes into subsets. It was decided to begin model development with data for products containing only Portland cement and pure toxic metal compounds containing barium, cadmium, chromium, copper, lead, nickel or zinc, as oxides, hydroxides, nitrates, or chlorides, separately or in combination. Eight literature references containing suitable information were identified from the database (Alford et. al., 1981, Bhatty et al., 1991, Diez et al., 1997, Hills and Ouki, 1999, Kindness et al., 1994, Stegemann et al., 1999, Zamorani et al., 1988 and 1989). For these references, Columns 2 and 3 of Table 2 show the number of different values of each variable reported, and the number of products for which this variable was measured. As 26 different single batch leaching tests were performed (counting the aliquots of an acid neutralisation capacity test as separate batch tests), the liquid-to-solid ratio (L/S) and acid addition of the tests (in meq/g dry wt) were included as variables.

Table 1
Summary of data collected for synthetic wastes and pure compounds

Type of	**Number of data entries for**				
Synthetic Waste	**Lit.R.**	**Wastes**	**Products**	**Physical Properties**	
Pure inorganic compounds and their mixtures	29	44	587	Bulk Density	254
				Drainable Water	101
				Specific Gravity	206
				UCS	805
				Other	187
Pure toxic metal compounds and their mixtures	36	46	506	Bulk Density	324
				Moisture Content	101
				Porosity	135
				UCS	798
				Other	178
Pure organic compounds and their mixtures	14	38	188	UCS	227
				Other	94
Mixtures of pure inorganic and organic compounds	4	4	35	Bulk Density	111
				UCS	126
				Other	143
Synthetic treated wastes	13	31	348	Bulk Density	238
				Moisture Content	199
				UCS	616
				Hydraulic Conductivity	126
				Other	121
Complex synthetic wastes	7	18	98	Total	65

Lit.R.= Literature References
UCS = Unconfined compressive strength

It is apparent from Table 2 that not all variables were measured for all products. In fact, for many of the variables, insufficient data for model development was available. Therefore modelling concentrated on prediction of the most common properties, unconfined compressive strength and leachate pH, on the basis of 15 variables related to the product preparation (shown in Column 4 of Table 2), with data sets of 123 and 427 points, respectively. The following equations from Tarassenko (1998),

$$J = \sqrt{IK} \tag{1}$$

$$W = (I+1)J + (J+1)K \tag{2}$$

with I= the number of inputs (15) and K= the number of outputs (1 or 2), allow calculation of the number of parallel cells in the hidden layer, J and the number of model parameters in a multilayer perceptron, W. Given the rule of thumb that the number of datapoints necessary to build a good model should lie between 3 times the number of inputs ($3I$=39) and 10 times the number of network weights ($10W$=1100), it appeared that the available quantity of data was sufficient. Of course, this rule of thumb presupposes that the information content of the inputs with regard to the outputs is high.

Table 2
Summary of data collected for 80 products from 8 references

Property	Number of		Input/Output
	Values	products	Variables
Portland cement (% of total dry mass)	80	80	input (1)
Water (% of total dry mass)	80	80	input (1)
Contaminant concentration (% dry solid) for Ba, Cd, Cr, Cu, Pb, Ni, Zn, Cl^-, NO_3^-	80	80	input (9)
Curing temperature (°C)	6	80	input (1)
Initial setting time (minutes)	27	27	
Final setting time (minutes)	18	18	
Age (days)	20	80	input (1)
Bulk density (g/cm^3)	88	33	
Moisture content (% wet wt)	38	38	
Specific gravity	31	31	
Porosity (% vol)	7	7	
Unconfined compressive strength (MPa)	123	40	output (1)
Flexural strength (MPa)	2	2	
Leaching tests (single batch extraction) characterised by L/S and acid addition	26	58	input (2)
Leachate pH	427	48	output (1)
Leachate Eh (mV)	222	22	
Leachate conductivity (mS/cm)	198	22	
Leachate concentrations (mg/L)	27	17	

For the unconfined compressive strength data set, 99 datapoints were used in neural network training, 12 datapoints were used for validation during the training process to prevent overfitting, and 12 previously unseen data points were used to test the performance of the final model.

For the pH data set, 299 data points were used for training, 64 datapoints were used for validation, and 64 datapoints were used to test final model performance.

3.2. Neural Network Analysis

Both the unconfined compressive strength data set and the pH data set were modelled with and without input variable selection. When all the variables were used to build a model, the sensitivity of the model to the individual variables was analysed.

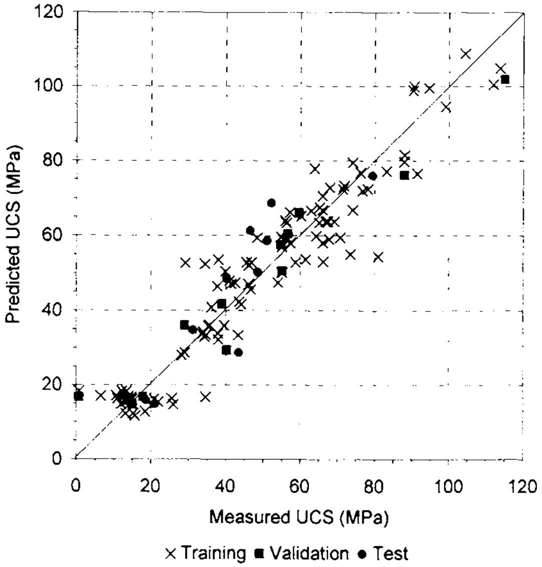

Figure 1. Predicted vs measured UCS for neural network model with 3 inputs.

Unconfined Compressive Strength

Figure 1 shows the predicted unconfined compressive strengths as a function of the measured values for the model developed using Trajan's input selection algorithm. The input variables selected were curing temperature, curing time, and water content. Using these variables alone, a multilayer perceptron model with six cells in the hidden layer was able to achieve correlation coefficients between the measured and predicted values of 0.95 for the training set, 0.97 for the validation set, and 0.92 for the test set.

The Trajan input selection algorithm tries to strike a balance between optimal model performance and minimising the number of input variables. In other words, the inputs it selects will have the greatest influence on model performance, but are not necessarily the only input variables that influence the output variable. Water content, curing time, and temperature are well known to be important variables for prediction of unconfined compressive strength. It seems that the effects of the toxic metal salts are small by comparison. Indeed, even when a neural network model (with three cells in the hidden layer) was constructed using all the input variables, it did not show improved performance, with correlation coefficients between the measured and predicted values of 0.94 for the training set, 0.96 for the validation set, and 0.95 for the test set. Analysis of the sensitivity of the model performance to the input variables resulted in the following ranking: curing temperature, water content, curing time, cement content, copper, zinc, barium, nitrate, chloride, lead, cadmium, chromium and nickel. Again, the first four variables are unsurprising. In addition, previous work with a portion of the data set, generated in a factorial design experiment

(Stegemann et al., 1999), showed that $Cu(OH)_2$ and $ZnCl_2$ act as retarders, whereas $Ba(OH)_2$, $Cd(OH)_2$, $Pb(NO_3)_2$ and $Ni(OH)_2$ were found to have no significant effect on setting or strength. The above ranking bears out these findings. The low ranking of chromium as a predictor of strength seems surprising at first, as it is well known to interfere with cement hydration (Mattus and Mattus, 1996). However, it seems that soluble chromium salts act as accelerators, whereas Cr_2O_3 is a retarder or has no effect. As chromium in both forms is represented in the dataset, chromium on its own is not a good predictor of strength. It is interesting to note that the model indicates that the strength of Portland cement products is approximately equally sensitive to nitrates and chlorides.

pH

Figure 2 shows the predicted pH values as a function of the measured values for the model developed using Trajan's input selection algorithm. The input variables selected were acid addition, curing time, cement content, nitrate, zinc, curing temperature and lead. Using these variables, a multilayer perceptron model with two cells in the hidden layer was able to achieve high correlation coefficients between the measured and predicted values of 0.98 for the training set, 0.99 for the validation set, and 0.99 for the test set. It is clear that the amount of acid added in the leaching test was rightly found by the variable selection algorithm to be the most important factor for prediction of pH, and cement content is also a variable of expected importance. Previous work with a portion of the data set (Stegemann et al., 1999) found $ZnCl_2$ and $Cr(NO_3)_3$ to be the dominant variables which affect the pH, with $Ba(OH)_2$, $Cd(OH)_2$, $Cu(OH)_2$ and $Pb(NO_3)_2$ also having a possible effect.

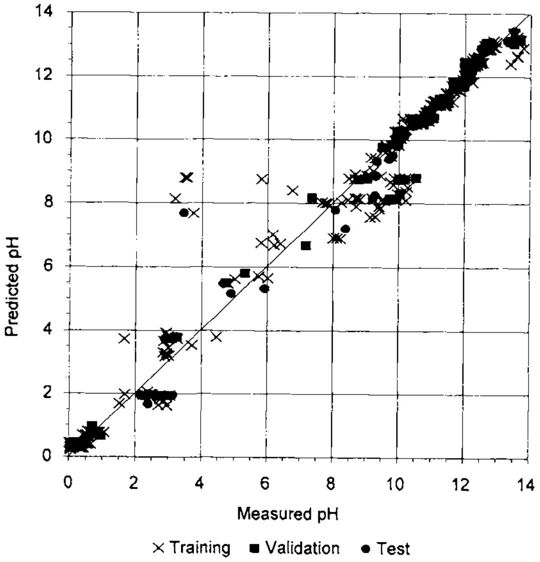

Figure 2. Predicted vs measured pH values for neural network model with 7 input variables

Use of all the input variables to construct a neural network model with four cells in the hidden layer resulted in correlation coefficients between the measured and predicted values for the training, validation and test sets of 0.99, 0.99, and 0.97. Sensitivity analysis of the model ranked the input variables as follows: acid addition, curing time, cement content, nitrate, zinc, water content, curing temperature, chromium, copper, liquid-to-solid ratio, barium, cadmium, lead, chloride, and nickel. In this dataset, chromium was not added as an oxide, so its effect would be expected to be more apparent (although in fact it is unknown whether the effect of chromium oxide on pH and acid neutralisation capacity is different than that of soluble chromium salts).

For both models, the model predictions were better for pH values greater than 10 and less than 3. Thus, the steep portion of the titration curve, which typically lies between 10 and 3 for cement/waste products, is not as well predicted, in the same way as the reproducibility of pH values measured in the laboratory tends to be poor in this range. In any case, the pH response to acid additions is of greater interest in the flatter region of the curve above pH 10.

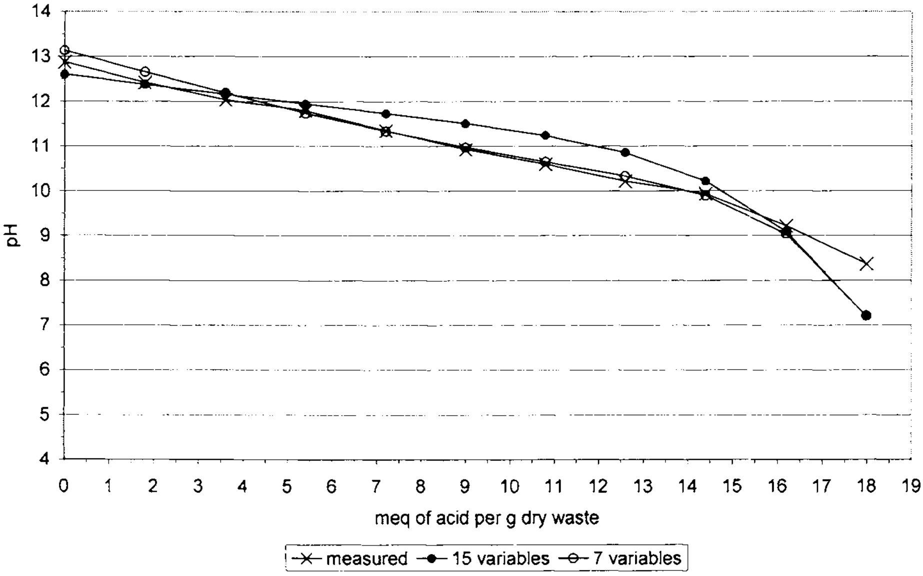

Figure 3. Measured and predicted titration curves for a solidified product containing seven heavy metal salts.

The average difference between the predicted and measured pH values was 0.4 pH units for both models, which is in the range of the interlaboratory reproducibility to be expected for an acid neutralisation capacity test (Stegemann and Côté, 1991). Figure 3 compares the measured titration curve for a product containing $Ba(OH)_2$, $Cd(OH)_2$, $Cr(NO_3)_3$, $Cu(OH)_2$, $Pb(NO_3)_2$, $Ni(OH)_2$, and $ZnCl_2$, which was part of the test set (i.e., not used in neural network training) with the curves predicted by the two neural networks.

4. CONCLUSIONS

Modelling of unconfined compressive strength data for Portland cement systems containing barium, cadmium, chromium, copper, lead, nickel or zinc, as oxides, hydroxides, nitrates, or chlorides, from 8 different literature sources using neural networks resulted in a high correlation between measured and predicted values. However, unconfined strength was found to be well predicted by using only well known predictors of unconfined compressive strength: curing temperature, curing time, and water content. It was not possible to improve the accuracy of prediction by including contaminant concentrations in the model, although a sensitivity analysis of the model developed using contaminant concentrations showed the expected sensitivities to these variables.

Neural network modelling of leachate pH was more successful, both in the sense that high correlations between measured and predicted values were obtained, and in that the effects of contaminants on pH and acid neutralisation capacity could be observed. The agreement between measured and predicted values was similar to that which might be expected for pH measurements in different laboratories.

Further work is being undertaken with data for synthetic wastes, to analyse larger data sets, including additional variables, such as other contaminants and binder types. The properties of greatest interest are those related to handling characteristics, durability and leachability, e.g. setting time, strength and pH. The ultimate goal is to be able to predict these properties for cement products containing real wastes.

The sensitivity of the neural network models to combinations of multiple variables is also being investigated, to gain a better understanding of interactions between complex wastes and cements.

ACKNOWLEDGEMENTS

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Re-use of abandoned coal mining waste deposits for the production of construction materials: a case of innovative tendering

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The Dutch Ministry of Transport, Public Works and Water Management, the Dutch Ministry of Agriculture, Environmental Preservation and Fisheries and the Dutch Province of Limburg all work together in the "Maaswerken" project. In this project several measures (river widening, deepening etc.) are being developed to enhance the discharge capacity of the river Maas (Meuse). Flood risk reduction and navigation improvement are the main targets of the "Maaswerken" project. "Grensmaas" is a particular part of this project and is aimed at (1) flood risk reduction, (2) gravel production and (3) nature development. The location for part of this project is between Maastricht and Roosteren in the Netherlands.

A survey of the area has revealed two large coal mining waste deposits: a 50,000 m^3 fly-ash deposit and a 210,000 m^3 mining (coal-washery) sludge deposit. The deposits are about 40 years old and both are remains of the former coal mining industry in the region. To fit in with the basic variant of the redesign plans for the bed of the river Maas, these deposits would have to be removed. Several options have been considered with regard to the removal and re-use of these coal mining waste deposits.

On the basis of their physical and chemical characteristics, the materials in both deposits seemed to be suitable for the production of construction materials. This use was considered to be the most sustainable as well as the economically best option for using this material. Firms were invited to tender for the excavation and re-use of the mining wastes. The tender was based on a so-called "design & construct"-contract. The tender will be awarded on the basis of pre-defined criteria, as described in this paper. The sustainability of the end-use of the excavated materials will be a particularly important factor in the awarding of the tender. A final decision has not yet been taken. One of the aims is to provide some insight into how public tenders for a project can stimulate sustainable re-use.

At the conference the latest news will be given about working methods that have been chosen and about the use that is to be made of the materials. If all preparations, tendering and contract-forming negotiations ron smoothly, the work may already have started by the time this conference begins.

1. INTRODUCTION

Large parts of the Dutch Maas valley were flooded in December 1993 and January 1995. Subsequently, a governmental advisory committee ("Boertien II") was asked to assess the situation and to recommend measures for reducing the risk of flooding. One of the committee's recommendations was an enlargement of the main channel of the Maas over a stretch of about 200 km. The main targets of the "Maaswerken" project are flood risk reduction and navigation improvement. A third objective is the development of ecological areas in the Maas valley. Several alternative ways of achieving these three objectives have been developed and have been elaborated in an environmental impact assessment (EIA) [1].

The measures needed to enlarge the channel of the Maas will involve the removal and handling of many materials, e.g. gravel, sand, contaminated sediments and waste materials. The "Maaswerken" project is likely to involve the removal of ca. 5 to 11 million cubic metres [2, 3] contaminated sediments and dredged sediments.

A river-widening project near Urmond and Grevenbicht has been planned. In order to realise this project a 50,000 m^3 fly-ash deposit, a 210,000 m^3 mining (coal-washery) sludge deposit, together with layer materials and various mixed materials will have to be removed. These deposits are about 40 years old and both are remains of the former coal mining industry in this region. The locations of these deposits are shown in the Figure 1 and 2 below.

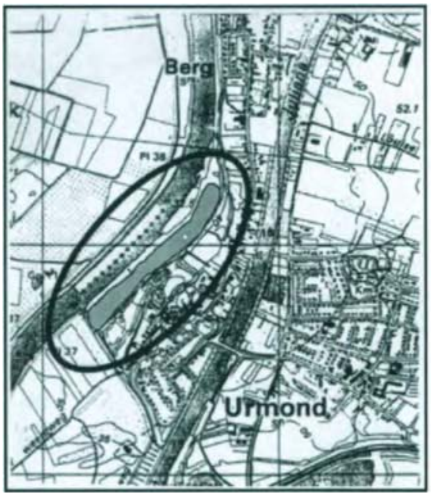

Figure 1: Deposit near Urmond

Figure 2 : Deposit near Grevenbicht

This paper focuses on how a new, sustainable destination is being sought for these materials.

2. POSSIBLE USES FOR FLY-ASH AND COAL WASHERY SLUDGE

2.1. Characteristics of the materials

The mining waste materials were analysed for contaminants, leaching behaviour, mineral composition and fuel characteristics [4]. A summary of the characteristics can be found in Table 1.

Table 1
Summary of the average quality coal washery sludge and fly ash

	coal washery sludge	fly ash
Fuel analyses		
Ash content (%)	81	84
Volatiles (%)	10	9.4
Humidity (%)	30	26.4
Organic content (%)	9.5	9.7
Caloric value dry (MJ/kg d.s.)	3.7	3.1
Caloric value wet (MJ/kg)	2.6	2.2
Combustion value wet (MJ/kg)	1.8	1.5
Mineral content after combustion		
SiO_2 (%)	58	58
Al_2O_3 (%)	18	14
CaO (%)	1.5	12
MgO (%)	3.3	1.7
Fe_2O_3 (%)	6.7	6.3
Total sulphur (%)	0.3	0.24
Particle size distribution		
< 2 μm (%)	20	17
< 63 μm (%)	31	45
Trace elements		
Cadmium (mg/kg dm)	9.1	7.9
Mercury (mg/kg dm)	1	0.73
Copper (mg/kg dm)	92	130
Nickel (mg/kg dm)	37	97
Lead (mg/kg dm)	234	135
Zinc (mg/kg dm)	600	810
Chromium (mg/kg dm)	43	58
Arsenic (mg/kg dm)	27	21
Barium (mg/kg dm)	318	144
Mineral oil (mg/kg dm)	1000	360
PAH (mg/kg dm)	20	9.5
Extr. Organic chlorides (mg/kg dm)	1	3.5
PCB (μg/kg dm)	52	175

2.2. Leaching characteristics and compatibility with the Dutch Building Materials Decree

The leaching characteristics of the material were investigated corresponding to the regulations laid down in the Dutch Building Material Decree [5]. The leaching test in accordance with the conform Dutch standard NEN 7343 proved that most heavy metals leach only very slightly (many below detection level). Only Sb, Se and sulphate showed leaching values approaching -but still below- the limits set by the Dutch Building Materials Decree. More important is the mineral oil content, which in many samples was above the maximum legal level for substances that are to be used in public works. It should be noted that the rules of the Dutch Building Materials Decree apply only to materials that are destined for direct use for public works.

2.3. Preliminary assessment of options

In our attempts to find possible uses for these coal mining waste deposits, we considered the following options:

- use of the deposits as construction material within the "Maaswerken" project;
- use of the deposits as construction material for other public works;
- use of the deposits as raw material for the production of construction materials, like cement and bricks;
- use of the deposits as auxiliary materials for the construction of landfills or pits for contaminated sediments;
- excavation and landfilling (or relocation of the deposits);
- a combination of these options.
-

All these options were carefully investigated with regard to their technical, economic, environmental and regulatory aspects. Local logistics and the sustainability of the options were also taken into consideration [4].

On the basis of the characteristics of the deposits (see table 1 and leaching characteristics, par. 2.2.) and as a result of discussions with the construction materials industry in a preliminary phase, it was concluded that these materials could serve as useful raw material for cement or brick production. This would make re-use of such materials sustainable and economically sound. Direct use as construction material for public works would be difficult because of the oil content of the materials.

3. INVITING TENDERS FOR THE PROJECT

3.1. Tender procedure

The procedure adopted is a European tender procedure with an open character and considerable freedom for contractors. It is similar to a "design & construct" procurement. To ensure a serious (and paid) effort by the contractors the tender starts with a primary selection of contractors and then divides the work into 6 separable steps/phases.

1. Submitting of contractors for the pre-qualification within a European tender (May 1999)
2. Selection of a maximum of 5 contractors on the basis of several criteria (May 1999)
3. Agreeing on the tender with these 5 contractors (June 1999)

4. Preparation of a detailed project plan and the finding of potential re-users of the mining waste materials by the contractors
5. Submission of final offers with specified plans and prices (December 1999)
6. Judging of the offers by various teams and acceptance of the best tender for the project.

For the pre-qualification, the contractors needed to submit informative documents that prove that the contractor:

- has (demonstrable) knowledge and experience in the field of soil-remediation above and below groundwater level;
- can handle a project of this sort and size;
- sees founded possibilities for beneficial re-use of the materials removed;
- is able to set up a team to organise such a project (possibly via a consortium);
- has a certified quality system.

Every (sub)criterion has its own weighting factor. Therefore all documents submitted received a total score. This lead to a ranking and the 5 best presentations were invited to tender for the project. For making an elaborate tender the contractors will receive a financial compensation of €55,000 (if a worthy project plan is presented).

The usual tender documents (e.g. basic data, Terms of Reference etc.) were submitted to the 5 parties. In the Terms of Reference several pre-conditions were specified. These included:

1. general requirements concerning excavating, processing, transport and end use of materials;
2. specific requirements concerning excavating;
3. requirements concerning excavating material and rolling-stock;
4. specific requirements concerning possible processing of materials;
5. specific requirements concerning possible cleaning of occasional percolate and draining water;
   e.g. cleaning methods and permits;
6. specific requirements relating to transport;
   - minimal hindrance to other traffic;
   - control and maintenance of roads and facilities;
7. requirements relating to the transport of material;
   - use of material only for *this* project;
8. permission of road-owner(s);
9. erosion;
   - means of preventing the erosion of contaminated material at the excavation site or from (temporary) depots into the river;
   - means of preventing the emission of contaminated material into the ground - or surface-water.
10. limits on the emission of noise, dust or other contaminants to the air.

In addition, a document containing general information about the location and materials was added to the tender documents.

With the 5 contractors who had obtained the pre-qualification, the tender procedure proceeded as follows.

Table 3
Planning of tender procedure

Month (1999)	activity
June	plenary enquiry session
July	bilateral enquiry session (for specific questions)
End of July	location visit
August – September	additional soil investigation
October	second plenary enquiry session
November	second bilateral enquiry session
December	final tendering

3.2. Additional investigation into soil and mining wastes

In the announcement inviting tenders it was stated that "Maaswerken" would order an additional soil investigation for the purpose of reducing uncertainties about the amount of material involved and about contaminants. The tendering contractors were informed about the scope of the additional investigation and about the methods to be used. Furthermore, excavated samples could, if requested, be made available to the tendering contractors so that they could conduct their own research on these samples.

The five pre-qualified contractors were invited to state their wishes regarding the additional investigation (e.g. sampling methods, specific analyses etc.). The wishes of the five contractors formed the basis for the investigation plan. Two independent soil investigation companies were instructed to carry out the investigation.

- The investigation consisted of: sampling at the locations via grit-planed drills and measurement of geophysical characteristics;
- digging of grooves (about 25 meters long, max. 5 meters deep and min. 2 meters wide) in order to get a visual picture of the composition of the soil and to provide the contractors with sufficient sample material. The contractors were invited to be present when the grooves were dug;
- analyses of physical, chemical, geotechnical and fuel characteristics of the various materials and analyses of the groundwater at various levels.

3.3. Enquiry sessions

Plenary enquiry sessions were held to give the contractors general information and to tell them how the Maaswerken project office envisaged the final situation. Bilateral enquiry sessions were held with each contractor individually in order to answer specific questions and to encourage creative solutions without having to withhold information because of presence of competitors.

3.4. Negotiations by contractors with third parties

In the period before December 1999 contractors had ample time to negotiate with end-users of the waste materials and with intermediaries (if any).

3.5. Ranking of the tenders

The five contractors were asked to elaborate on several aspects on which the different tenders would be judged and which will, besides price, be the basis for the final selection of the contractor to whom the project would be granted. Each aspect was scored separately.

Several proposals have now been received from all 5 contractors. Two contractors proposed alternatives, which did not comply with the Terms of Reference. These alternatives proposed (1) a different (temporary) depot in the area (as well on land as in the Maas basin) for the excavated materials and (2) instead of removing of the coal mining waste, isolation at the location.

Different teams scored the tenders independently without knowing the prices connected with the specific proposals.

Two teams studied the technical aspects independently (70% of the total weighting factors), 1 team judged the general permit plan (20% weighting factor) and 1 team saw to the organisation and judged the feasibility within the terms indicated.

Criteria	weighting factor	sub aspect
Realisation methods	20%	techniques; safety; health; hindrance caused by activities on site (noise, dust, vibrations, transport, parking, etc.)
Environmentally sound end-use of materials	30%	sustainability
Environmentally sound method of excavating	10%	emissions to soil, water and air
Permits according to general permit plan	20%	uncertainties in permit planning and procedural issues
Organisation	5%	process (tasks, qualifications and responsibilities); staffing; scheduling; flexibility
Feasibility of realisation according to provisional time-schedule	5%	
Transport	10%	safety; logistics; hindrance (caused outside the project-site)
Total	100%	

3.5.1. Scoring of realisation methods

It was made clear beforehand that an inadequate score on the end-use aspect would immediately lead to rejection of the tender. Definitive disposal of or landfilling by all excavated materials would lead to an absolute minimum, but adequate score. Use as construction material, for, say, sound barriers would lead to a better score.

3.5.2. Assessment of end-use of materials

It is common policy that the environmentally sound re-use of materials is preferred, the same holds with regard to the materials excavated in this project. As stated earlier, there are various ways in which the materials can be used beneficially. Beneficial use of (part of) the materials is rewarded, it is given a higher score than simple (definitive) dumping of materials. The temporary deposition of the material (at another location) scores higher, because this increases the probability that the material will be used in a sound way in the future. Controlled use in sound barriers is judged in a similar way. The highest scores are awarded to the most sustainable uses that will replace the use of primary materials and will lead to use in long-lasting and high-value construction materials, e.g. as a secondary raw material for building materials (bricks, cement).

3.5.3 Judging the method of excavating

This criterion deals mainly with the effects on the environment and on persons living close to the site. Emissions to ground and groundwater, the air and water as a result of activities on the excavation-site are judged on their nature and their size, as are the measures that the contractor plans to use to diminish these emissions. The moisturising of roads for instance to prevent dust-emission was judged positively. Also the purification of wastewater or directing it to a nearby regional treatment plant would be favoured.

3.5.4. Scoring of permit planning

The assessment team checked whether all permits needed were anticipated in the plan and whether there was a strategy for obtaining these permits. Items scored were the extent to which they were compatible with procedures that had already started and the reasonable certainty that the required permits could be obtained in time.

3.5.5. Scoring of organisation

The assessment team judged how the contractor had planned to organise this specific project. The organisation scheme and the underlying vision for this specific project were studied as were the submitted list of key staff and their background experience (c.v.'s). The quality insurance plan, feasibility of the schedules, use of hardware within hindrance limits are also of importance.

3.5.6. Feasibility within the provisional schedule

A few restrictions make the execution of the project difficult at both locations. The project needs to be completed between the period when the permits are awarded and the 1st of November 2001, because of financial pre-conditions.

Difficulties include the higher water levels in the Maas in wintertime, which can sometimes interfere the excavation and the conditions of de River Law-permit, which forbids temporary depots (above local ground level) in the winter period. Use of more equipment at the same time is limited by maximum noise levels and the maximum number of lorries allowed on local roads. The proposals were judged by the way in which the contractor dealt with this matter.

3.5.7 Scoring of aspects of transport

Means of transport and hindrance were scored (a ship scores better than lorries passing through populated areas). Aspects are the type of transport material (lorries, ships, use of conveyor belts), choice of transport routes, frequency of transport movements and maintenance of local roads (because of the destructive effect of many heavy lorries per day).

3.5.8. Scoring of alternatives not complying with the Terms of Reference

One contractor offered 2 alternatives and another contractor offered one alternative, all deviating from the Terms of Reference. The contracting parties were allowed to offer alternatives and these proposals were therefore judged. Because of the high quality and financial advantages of these alternatives, these proposals were scored in the same way as the other proposals. However, in this case the inviting party would have to deal with a change of starting-points.

3.5.9. Scoring of costs

A special problem in this method of tendering for a project (in which the contractor may choose different ways of handling the various materials) is that every contractor will use different amounts of material as the basis for cost calculations. The comparison was made easier because the contractor was asked to specify the costs with regard to each type of material separately (coal washery sludge and fly ash, cover material (clay, sand) and mixed material).

The bidding contractors were asked to give a fixed price regardless of the amounts of each material. It was assumed that this was possible because of the available soil-investigation and the influence the contractors had on these investigations. Furthermore the contractors selected were given the choice, for each of the material types, to offer a removal price per tonne (including end-use) for a wide range of amounts of material (or in other words: a price graph in which the price per tonne is a function of the amounts (in tonnes) to be handled).

The party inviting to the tender (the project office) determines the uncertainty in the total costs and determines the comparison value of each tender. Probability densities are determined for each material flow, via a Monte Carlo simulation [8]. The probabilities for each tender are compared with each other and with the fixed-price offers. Fixed price offers are compared with the 70% quantile of the non-fixed price expectation, because of preference that the project office has for a fixed-price offer and the increase of costs for projectmanagement and related risks.

3.6. Final assessment of tenders submitted

An overview of the tenders with their bid prices and the scores is now being prepared.

A few tenders are judged to be technically outstanding. Some are conformed to the Terms of Reference and alternatives are not.

In one of the alternative proposals the coal mine deposits and fly ash from both locations are gathered and stored isolated and controlled under groundwater level in such a way that the planned river widening remains possible at both locations (one of the terms). In that case the stored materials will remain available for future use by the building material industry. Although materials will not be re-used in this project, this alternative was given a high score because the proposal was technically very detailed and explicit, resulting in a good overall score. Moreover, the price was very attractive, because in the other tenders (in which the materials are re-used) end users pay very low prices for the materials (sometimes even negative). These tenders are relatively expensive. Apparently the local raw material market for the building material industry does not have enough demand at this moment. If this demand would grow in the future, then the stored materials are still available for re-use.

All proposals contain a few risks of a juridical nature (classification of the excavated materials, granting of permit requests) and of a technical nature (are the proposed techniques feasible?). However, the judging teams are confident of successful realisation if the project will be awarded to one of these contractors.

The judging teams have given their advice to the management of the Maaswerken project office. The decision about which contractor will be awarded the project has still to be made. At this moment not much information can be given with regard to how the project will proceed. At the conference we expect to tell you more.

4. OUTLOOK

At present (January 2000) there is still uncertainty about further follow up of the project. However, some general observations can be made:

1. The short time periods for completing the project are no longer applicable (the earlier applicable financial pre-conditions have been dropped). Now there is more time e.g. for permit procedures, for a contractor to negotiate with potential end-users and for development of more ingenious realisation plans.
2. The Dutch government has now decided that the expenditure on the design for restructuring the Maas river bed is to be reconsidered. At the conference we will tell you the latest developments.

5. CONCLUSIONS

1. The "design & construct" tender model is a useful basis for a project tender because:
    - tendering can be done on the open market, which will result in competitive costs;
    - contractors are not bound to rigid, detailed Terms of Reference, contractors have the opportunity to use their creativity and show their specific expertise;
    - a range of different ways of realising the project is put forward, including ways that were not thought of beforehand;
    - it is still possible to choose the best tender in a unique way.
2. The project plans submitted show that a sustainable re-use of this material is possible.
3. The contractors did not yet succeed in making a plan in which the coal mining wastes are to be re-used that could compete on costs with a variant where the coal mining wastes are to be stored, isolated and controlled. Apparently the local raw material market for the building material industry did not have enough demand at this moment. If this demand would grow in the future, the then stored materials are still available for re-use.
4. The tender procedure resulted in different proposals from various contractors, each with his own specific knowledge and expertise and views on how to solve a difficult situation at the lowest costs and each using his specific business contacts to negotiate the end-use. Moreover, the contractors seemed to enjoy being stimulated to put their own thoughts, expertise, techniques and style into this project and being able to use their own business contacts in the market.
5. Innovative and environmentally better solutions could be chosen by the party inviting the tender because of the large range of variants offered. The traditional type of tender would have led to fewer options.
6. Because of the innovative nature of the solutions offered, more juridical and technical uncertainties were introduced.
7. The project has shown us that a "design & construct" tender procedure has considerable potential and, if there is good understanding with the contracting parties, it can lead to innovative and better solutions for complex (and expensive) environmental problems.

6. RECOMMENDATIONS

A few items for optimising the "design & construct" tender procedure are currently under consideration.

1. The tender procedure should allow contractors enough time to negotiate with intermediaries and end-users.
2. Applications for permits that are likely to take a long time process are to be submitted as soon as possible so that there is certainty that the permits will be granted in time. In some cases the permit procedures can be started in advance. The project plan can be submitted to the permit procedures later, which can save a considerable amount of time.
3. It is important that each member of the project team of the inviting party has his or her own specified tasks. These members need to be available during the whole tender procedure.

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Waste Materials in Construction
G.R. Woolley, J.J.M. Goumans and P.J. Wainwright (Editors)

CONSTRUCTION WASTE CHARACTERISATION FOR PRODUCTION OF RECYCLED AGGREGATE – SALVADOR/BRAZIL

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The continuous growth of municipal solid waste generation, especially from construction activities, has been responsible for the appearance of many and efficient municipal solid waste management policies from public authorities. An efficient waste management program can avoid inappropriate waste disposal, which can cause damage to both environmental and public health. Additionally, it may even lead to the development of recycling programmes.

Giving special attention to solid waste from civil construction enterprises, it is important to develop environmentally active practices among construction companies with a view to reduce waste generation, increase reuse and recycling. In order to develop alternatives for construction wastes recycling, it is important to provide efficient solid waste characterization studies.

An experimental study has been carried out in the city of Salvador, Brazil. Currently, 1450 tons daily of construction and demolition (C&D) wastes has been generated in Salvador. Solid waste has variable physical characteristics that depend on the construction sector involved, the techniques employed, the construction phase and the social-economic characteristics present in the urban area in question.

This paper presents the results of an intensive study of construction and demolition wastes from Salvador with the intention of creating alternative methods of increasing environmental protection and generation of low price raw material by recycling solid waste. The principal

procedure used involves the characterisation of solid waste according to its physical characteristics and social-economic aspects.
The results of this characterisation identified priority research lines that will help to maximise recycling of C&D waste produced in Salvador and help develop a local construction material market.

1. INTRODUCTION

The large amount of general waste produced every day is one of the main problems in urban areas. Construction and demolition wastes are one of the key aspects of this subject.
Population growth of and consequent increase in urban construction lies behind a chronic problem, which is the vast production of construction and demolition (C&D) wastes. Thus, the necessity of finding appropriate solutions to C&D waste destination is becoming quite clear and recycling appears as a profitable alternative that will increase the lifetime of landfills and reduce exploration of natural resources.
In many developing countries C&D wastes have often been disposed incorrectly in areas such as vacant urban lots and water streams courses. This behaviour has produced several environmental / health damages with waste materials of high recycling potential. In other countries, to minimize those problems, public authorities have been adopting more restrictive and efficient wastes management policies. Several management policies have been developed with a priority view of reduction, recycling and reuse of waste.
As a matter of fact, the Municipal Waste Management Company of Salvador-Brazil (LIMPURB) has recently created the "C&D Waste Management Program". The main goal of this program is to correct urban disturbances generated by illegal disposal of construction and demolition wastes in Salvador and on its outskirts.
The installation of C&D waste Recycling Plants is also part of this program. These plants will process construction waste, producing low price aggregates to be used as raw construction materials. These recycled materials should be used to provide social benefits in low income areas of Salvador by installing new urban infrastructure (pavements, drainage, etc.) and low cost buildings.
For the success of the C&D waste Management Program, it is necessary to emphasise that C&D waste show quite particular characteristics. The main properties of C&D waste, especially composition and amount, are affected by the great variety of raw construction materials, techniques and methodology usually employed in construction process.
Therefore, the developing stage of local civil construction (labour qualification, construction techniques applied, etc.) influences directly C&D waste composition. In this way the waste characterization is an important step in the study of C&D wastes.
This paper presents the methodology and the results of Salvador's C&D wastes characterization program, including social, material, and operational aspects. This study analyses the potential of Salvador waste recycling in order to produce low cost construction materials. A summary of Salvador's C&D Waste Management Program and some considerations about the use of processed debris as construction materials are also presented.

2. SALVADOR'S C&D WASTE MANAGEMENT PROGRAM

Salvador's C&D waste management program aims at the adoption of an ordering policy which limits environmental degradation by reducing waste generation, increasing C&D waste reuse and recycling and, in general, integrating all the diverse agents involved in the C&D waste management process.
The C&D Waste Management program for Salvador shall promote reduction of municipal waste collecting costs by the minimisation of corrective urban cleaner activities or by the production of low cost recycled materials.
One of the main structuring principals of this project is the decentralisation of C&D waste reception and final disposal. To achieve this, a number of strategically located areas were prepared to receive those materials. They are called C&D Waste Disposal Sites (WDS) and C&D Waste Disposal Bases (WDB).
Twenty-two disposal sites are planned (six in operation at the moment) receiving and transferring C&D waste originating from small generators. Five bases will also receive, reuse and recycle this material. Beyond that, the project intends to implant environmental educational programs, impede clandestine disposals and monitor late illegal disposal sites with the aim of eliminating inappropriate C&D waste dumping. Also foreseen is the stimulation of correct disposal and recuperation of areas degraded by inappropriate disposal of C&D waste. Figure 1 shows the simplified flow chart of Salvador's C&D Waste Management Program.

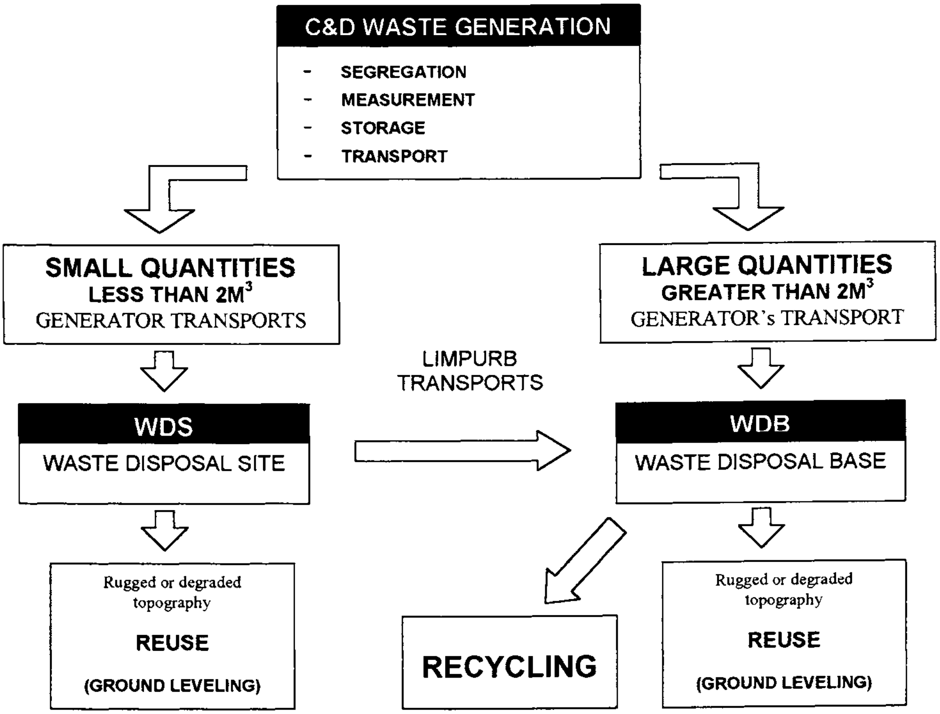

Figure 1 – Simplified flow chart of Salvador's C&D Waste Management Program

This program also aims topographical correction and degraded areas recovery in WDSs and WDBs. The key of this program is the creation of Recycling Plants at the WDBs. Each plant will process (crush and sieve) at least 200 tonnes daily of C&D wastes from Salvador. The processed debris will be commercialised as aggregate and used as social construction materials.

The *Waste Disposal Sites*_will be placed next to C&D waste generating areas. WDSs implantation areas must be chosen preferentially between those that are already used as waste settlings. They will be able to receive by each generator up to 2m^3 of waste per day. If a generator exceeds this limit, the WDS's staff will indicate the nearest BASE where larger quantities of waste should be delivered. At each WDS's the material will be temporarily stocked and then transported to a Waste Disposal Base where reuse or final disposal will occur.

The *Waste Disposal Bases* will be placed near C&D waste generating centre areas, intending to receive, reuse and recycle large volumes of C&D waste. This material will come from WDSs and generators who produces more than 2m^3 / day. These areas must be chosen between those with uneven topography or previously degraded areas.

3. CONSTRUCTION & DEMOLITION WASTE FROM SALVADOR

Currently, the amount of C&D waste collected in Salvador is about 1453 tons / day. This tonnage consists of 41% of the total urban waste collected by LIMPURB in Salvador. Nevertheless, this is only part of the total waste generated. It is estimated that at least 250 tons of waste goes uncollected every day.

The population growth is an important factor that has directly contributed to the increase of the urban waste production. In particular, the high deficit in habitation creates pressure for new housing and the resulting expansion in the number of homes being built increases C&D waste generation notably.

Figure 2 shows the evolution of the C&D waste collection in Salvador for the last 11 years. It shows that between 1996 and 1998 there was a enormous increase in this material collection. This fact is seen as a result of the "C&D waste Management Program", which contributes to the reduction of inadequate and illegal disposal of this kind of waste.

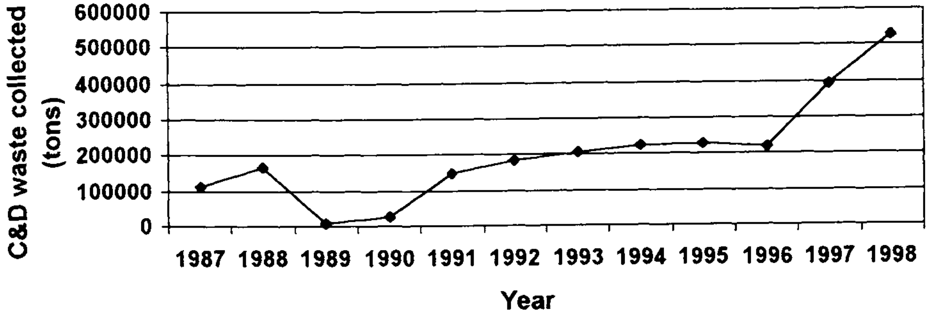

Figure 2 – Evolution of C&D Waste collecting in Salvador (LIMPURB, 1998)

4. CHARACTERISATION METHODOLOGY

C&D wastes characterisation is a fundamental stage in helping to identify alternatives to reduce / reuse and recycle. Precise knowledge of waste properties expands opportunities to maximise its utilisation as recycled construction materials.

In Salvador, the characterization of the C&D waste was done by the partnership between LIMPURB and GEMAC / UFBA (Group of Studies in Construction Materials of the Federal University of Bahia) in September / October 1999. Field studies were carried out at Canabrava landfill site in Salvador.

The methodology used to characterise Salvador's C&D wastes followed the procedures of: sampling, receiving, homogenising, quartering and testing analysis as described below:

4.1. Sampling, Receiving, Homogenising and Quartering

C&D waste samples were collected at both waste disposal sites and Canabrava Landfill. Sixteen C&D waste samples (estimated amount of 142,000 tonnes) were analysed. This tonnage represents 10% of Salvador's daily C&D waste generation, which represents an reliable amount for the statistical work in this study.

The samples were analysed considering aspects related to both delivery site (WSD and landfill) and the income level of generating areas of Salvador's C&D waste (low, medium and high).

The first step was to remove an initial sample between 5 and 10 tonnes from the desired C&D waste and do a first sample reduction. Then, the material was mixed to form homogenous groups, followed by consecutive quartering to obtain a sample weighing about 500 kg. Figure 3 shows the flow chart of this process.

4.2. C&D Characterisation Tests

- Size distribution - The final sample was screened through 50 mm, 25 mm and 4.8 mm sieves. Each retained fraction was weighted. Through this method waste was classified into 4 different sizes. This procedure follows the recommendation of Brazilian Standard NBR 7217.

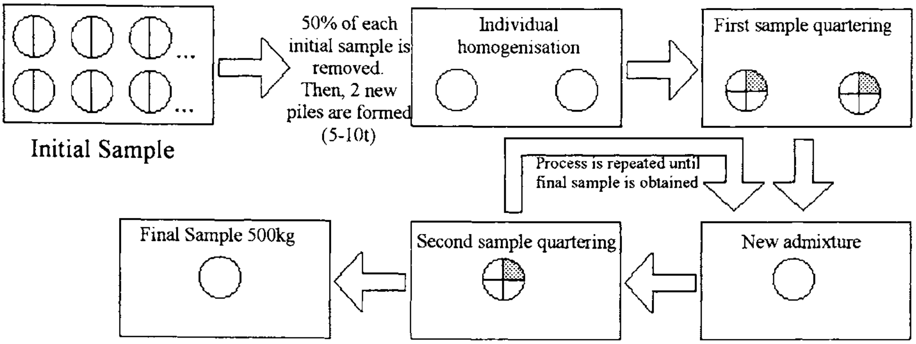

Figure 3 – Flow chart of Salvador's C&D waste sampling process

- Gravimetric composition - The waste's gravimetric composition was determined by classifying the material types of each fraction of the screening process. Those elements composed by more than one kind of material were classified according to predominance. The materials classification was done following the groups below:

1 – soil and sand
2 – white ceramic
3 – red ceramic
4 – asphalt
5 – concrete and mortar
6 - stone
7 – reinforced concrete
8 – metals
9 – gypsum
10 – leather and fabrics
11 - plastic and rubber
12 - paper
13 - timber
14 - other material

5. RESULTS

According to the methodology presented, figure 4 shows the size distribution and figure 5 the main components analysis of Salvador's C&D waste.

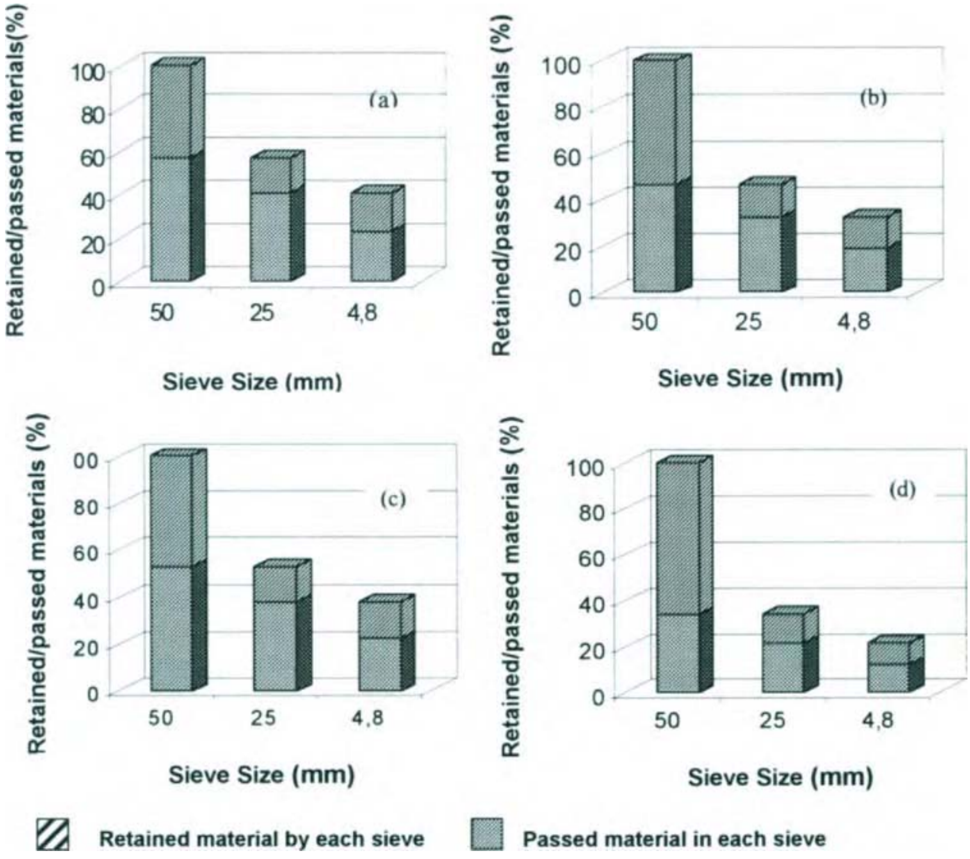

Figure 4 –Size distribution of Salvador's C&D wastes
(a) WDS; (b) Delivered at landfill; (c) Low & medium income areas; (d) High income areas

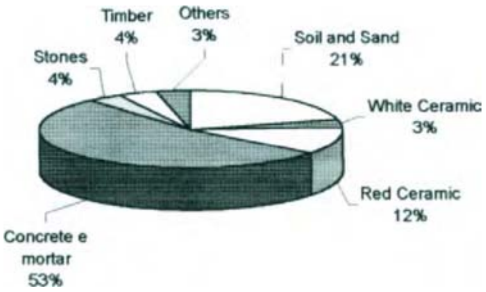

Figure 5 – Main components of Salvador's C&D wastes

The analysis of figure 4 indicates:

- Parts greater than 50mm occupy the majority of C&D waste in Salvador. Whereas the remaining particle sizes were well distributed on the other sieves.
- The C&D wastes size distribution found in high-income areas is similar to the one delivered at landfill. Both distributions have a low amount of small materials (passed through 4,8mm sieve) and high percentage of large pieces (up to 66% of the material was retained in 50mm sieve). This similarity is quite understandable, as the C&D waste sent to landfill came from high-income areas. People in these areas can afford the delivery costs and most construction companies concentrate their building activities in high-income areas.
- On the other hand, the size distribution of C&D waste from low/medium income areas of Salvador is similar to the ones collected at WDSs. This similarity establishes the main strategy of the WDSs, which collect waste from auto-construction activities and small house repairs (typical activities of low/medium income population on the Salvador area). Due to the high transportation cost to official the landfill sites, these wastes typically found there way onto vacant urban lots and into watercourses. In 1996 there were 420 illegal C&D waste disposal sites identified in Salvador. With the creation of the Waste Delivery Sites and stronger policing of uncontrolled sites there was a significant reduction in illegal dumping (140 sites in 1998).

The analysis of figure 5 indicates:

- Concrete and mortars represents the major portion of Salvador's C&D wastes (53%). It is also significant the amount of ceramic materials (15%). These two groups, together with stones (4%) represent 72% of the samples studied. Those materials when processed (crushed and sieved) produce an aggregate with high potential for use on road construction and non-structural concretes.
- Soil and sand (21%) are also a significant part of Salvador's C&D wastes. The quantities of this materials will increase when larger pieces of debris are crushed in the recycling plants. Looking forward, some applications that use this fraction of the C&D waste should be studied. The Federal University of Bahia (UFBA), supported by Caixa Econômica Federal (Federal Bank for Urban Infra Structure and Habitation), is

carrying out studies to promote the use of these alternative construction materials as base and sub-base for roads as well as to produce soil-cement blocks and mortars. These applications should contribute to reduce the cost of construction in some areas of Brazil.

- Timber represents 4% of the waste under study, so it is possible to conclude that 21000 tonnes of high potential recycling material has been thrown away every year. In the C&D waste recycling plant, timber will be sorted at an early stage of the process and commercialised.
- Other materials (metals, paper, plastic, rubber, asphalt, gypsum, leathers, fabric, etc.) represent only 3% of Salvador's C&D waste. However, some components (such as gypsum, asphalt, clay, some paints and timber), even in small amounts, may cause damage to concretes and mortars if included as part of the aggregate (GEHO, 1997).

The composition of C&D waste will normally differ depending on the generation area / country, type of raw material used, construction techniques and other factors. Furthermore, the methodology used to characterise the waste may change the results considerably. Table 1 shows the main components of C&D wastes produced in different cities/countries. This table indicates the immense variation of the main components found in C&D waste.

Table 1
The main components of C&D waste of several cities / countries (% of weight)

MATERIAL	ORIGIN SITES						
	United Kingdom[1]	Hong Kong[2]	*Salvador**	São Paulo*[3]	São Paulo*[4]	São Carlos*[5]	Ribeirão Preto*[6]
Concrete and mortar	9	8	*53*	63	11	69	89
Soil and sand	75**	19	*21*	-	83**	-	18
Ceramic	5	12	*15*	29	3	30	23
Stones	-	23	*4*	-	-	1	-
Others	11	38	*7*	8	3	-	-

[1] Industry and Environment, 1996
[2] Hong Kong Polytechnic, 1993
[3] Pinto, 1994 (sample collect construction site)
[4] Castro, 1998
[5] Pinto, 1989
[6] Zordan e Paulon, 1997

* Brazil
** Soil, sand and stones

6. SOME APPLICATIONS FOR SALVADOR'S PROCESSED DEBRIS

Recycling and reusing C&D processed debris as an alternative construction material appears to be an interesting solution for the problems caused by its inadequate disposal. Some priority R&D fields were identified for Salvador C&D waste:

6.1. Production of Soil-Cement Blocks using processed debris

The use of processed debris to produce blocks with soil-cement is clearly a good alternative solution for this environmental problem and it also has the benefit of producing a low-cost construction material.

The possibility of making soil-cement blocks with processed construction waste presents several economic advantages: the production unit occupies little space, it requires few investments in industrial equipment and causes no environmental damage.

GEMAC/UFBA is studying the influence of the construction waste's composition in the production of blocks with soil-cement including how effects differ with partial or total substitution of soil by waste. The results obtained in this investigation should provide an appropriate solution for developing low cost housing.

6.2. Application of processed debris in base and sub-base of roads

One of the most widespread ways to use recycled debris is both in base and sub-base layers. Using debris in the flexible-granular bases and sub-bases of roads presents many advantages; firstly, this kind of recycling requires very simple technology and secondly it uses large amounts of material.

Moreover, previous researches show that the use of processed debris in various layers of roads is viable (HENDRIKS, 1998). However, debris may present significant differences of characteristics, according to each region. This makes research into local material necessary to establish technical and economic viability for the use of each region's waste material.

GEMAC/UFBA is developing studies of the behaviour of Salvador's processed debris behaviour in flexible-granular base and sub-base layers of urban roads. The results obtained will allow a maximum use of debris and will help persuade local contractors to accept processed debris as secondary raw materials in the road construction.

6.3. Production of Mortar and Concrete using additions of processed debris

Mortar and concrete can be produced using the waste material processed by a recycling plant. The equipment crushes the debris so that it can be used to replace part of the aggregates in the production of mortars and non-structural concretes.

The addiction of processed debris may increase compressive strength of mortars and concretes. This is caused by the natural pozzolanic effect of crushed debris, which also causes a tendency to reduce the consumption of clusters in relation to conventional dosages (LEVY & HELENE, 1998). This way, use of processed debris shows economic advantages both lower cost of recycled aggregates and reduction of conventional clusters consumption. On the other hand, mortars produced with processed waste may develop fissures, probably caused by the large quantity of fine particles found in this material.

GEMAC/UFBA is analysing different dosages of processed debris in mortar and non-structural concrete. The studies of final product behaviour consider workability, durability, strength and others. Finally, its economic viability is also verified.

7. CONCLUSIONS

- Salvador's C&D waste characterisation was a fundamental stage in the studying and planning of ways to reduce, reuse and recycle this material. This study has helped to identify ways to maximize the utilization of Salvador's C&D waste as recycled aggregate.
- This study has shown that Salvador C&D waste is a high potential recycling material for the production of aggregates. The recycling of this waste will reduce environmental damages caused by incorrect disposal, extend the useful life of landfills and preserve finite natural resources.
- The characterisation of Salvador's C&D wastes will continue to be done systematically by LIMPURB and GEMAC/UFBA, in order to analyse the variation of properties found over time and in different seasons of the year.
- At the present time, GEMAC/UFBA is studying the complete characterisation of the processed C&D waste of Salvador. This study analyses physical / chemical properties of the processed debris as aggregates for construction materials and the environmental risk it presents during the entire life cycle of the material.

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This paper is dedicated in memory of
Prof. José C. Cassa – 1st Coordinator of GEMAC

Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Solid Urban Wastes Minimization and Energy Conservation – A Challenge for the 21st Century in Brazil

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This work focuses on the minimization of urban solid wastes and energy conservation aimed at sustainable development. The minimization of urban solid wastes is related to efficient material resource utilization and helps to solve the problem of the shortage of available garbage disposal areas in great urban centers. On the other hand, energy conservation can be an alternative when the lack of investment in the electrical sector would otherwise restrict the continued economic growth of the country.

There are many ways of adequately dealing with urban solid wastes. For example, one can list the composting of organic wastes, recycling of materials, incineration of materials and the reduction in the amount of waste actually generated. In this paper, each of these options is evaluated and linked to energy conservation, in an attempt to show that it is necessary to consider all of these topics in order to construct a sustainable development model.

1. INTRODUCTION

Until the 1950's, economic growth had continued without concern for the emission of pollutants into the atmosphere or rivers. There were no restrictions, public opinion had little influence and the existing legislation was weak.

In the 1960's, environmental issues became more important. Emphasis focused on the correction of problems and deviations assumed great importance through sanitary engineering. Where pollutant emissions into the atmosphere were above tolerable values, filters were installed; where pollutants flowed into rivers, its streams were treated; when the wastes were solid, confinement and disposal were recommended.

Later on, concepts of efficiency, quality and productivity became important. Cost reduction in assembly lines, decrease in emissions of residues through reutilization techniques or recycling of residues became prominent.

From the 1980's to present day, the ideal of the prevention and minimization of waste generation were strengthened. Prevention and minimization of residues became as important as recycling or reutilization. Through the revision of production procedures, technological advances and the improvement in management practices, the prevention and minimization of residues came to be applied with the objective of making the production processes more efficient.

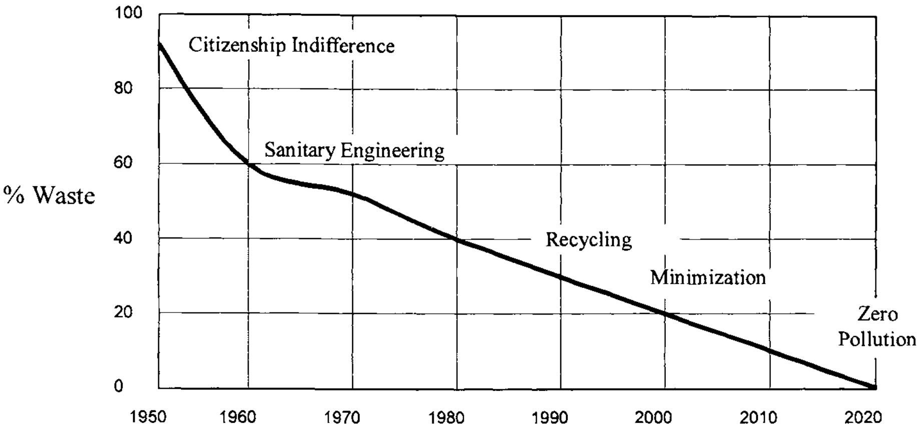

Figure 1: Industrial Solid Waste Generation Trend

More recently, the concept of "Zero Pollution" has been an objective of studies and of new approaches by the industry. The "zero pollution" philosophy is concerned with the reduction of pollutant emissions down to near zero level. Through recovery and reutilization, industries realized that there are residues that can be sold as raw material for other industries. Performance within the whole chain of the productive cycle of the product can be improved.

Figure 1 illustrates the scenario of the treatment of wastes generation for industry up to the 21st century.

In this paper, the concept of "Wastes Minimization", is applied to "urban solid wastes", or "USW", referring to the garbage generated in the urban centers due to residential activities. As in industry, where the concept of "wastes minimization" includes recovering, recycling and reduction, 'minimization of Urban Solid Wastes' includes waste reduction at source, recycling of materials, incineration and the composting of residues.

Similar to the evolution of the concept of "residues minimization", it can be said that Brazil is at the beginning of an apprenticeship for the "recycling of materials" shown in Figure 1. Nowadays, it is common to see advertising campaigns or to read reports on the benefits and importance of recycling materials. The same does not apply to the minimization of garbage generation.

Table 1
GDP per capita – selected countries.

Country	*GDP per capita (US$)*
Canada	19.380
USA	26.980
Europe and Central Asia	2.220
Middle East and N. Africa	11.021
Latin America and Caribbean	3.320

But the objective of this work is not to analyze the subject of the minimization of RSU exclusively. As will be seen, the adopted treatment of garbage, recycling, recovery of materials, reduction in source and minimization of residues contribute to the conservation of energy and are fundamental for the promotion of a model of sustainable development.

2. ENERGY AND GENERATION OF USW

Characteristics of different energy consumption exist for developed countries and poor countries. The Table 1 shows per capita GDP of some selected countries and the Figure 2 presents a graph with the consumption of primary energy of these countries.

Qualitatively, it can be seen from Figure 2 that developing countries' consumption of primary energy is less than that of the industrialized countries.

Canada and the USA are the countries that consume more primary energy for inhabitant, being represented by an elevated per capita GDP.

In general (in single logic), the economic growth of a country is accompanied by urbanization, industrialization and the increase in the consumption of material goods. In the limit sometimes means increase of comfort and increase of needing of the individuals satisfaction that are part of the nation. Besides the life expectation and the incidence of adult illiteracy are also better in the countries that consume more energy.

Another fact to note is that the level of energy consumption is also related to the hunger problems, habitation, health and education. The less the problem the higher is the tendency for high consumption of energy.

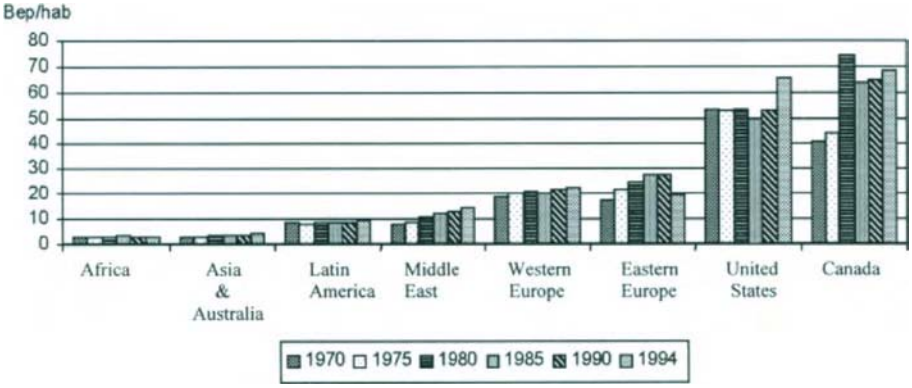

Figure 2. Evolution of the consumption of primary energy - selected countries
Source: OLADE 1996

Table 2
Generation of per capita garbage in some countries and cities

Countries or group of countries	kg/day	Cities of the world kg/day	kg/day
Canada	1.9	Mexico	0.9
USA	1.5	Rio de Janeiro	0.9
Holland	1.3	Buenos Aires	0.8
Swiss	1.2	San Jose	0.7
Japan	1.0	San Salvador	0.7
Europe	0.9	Tegucigalpa	0.5
India	0.4	Lima	0.5

Fonte: Emplasa, 1986 / OMS 1991, Neder [05]

Thus, it can be assumed that the level of energy consumption in Brazil will accompany economic growth.

To supply the demand of energy for the development of the country, Brazil has the advantage of possessing a favorable hydrology, which means hydroelectricity is the primary source of energy consumed in the country. Even so, the expansion of the electric system is related to the subjects of environmental order, besides depending on the existence of financial resources.

According to 1991 data, garbage generation per capita in some countries was as shown in the Table 2.

Referring to values of Table 1 and Figure 2, it can be observed that Canada and USA possess high per capita income, they present high consumption of energy and they produce a lot of garbage, relative to the other countries.

In general, the higher the level of income of the population, the higher the consumption of energy and the higher the amount of garbage generated by each inhabitant (see Figure 3). It should be said however, that the garbage generation is not considered a problem until the limit of the capacity of its appropriate treatment is reached.

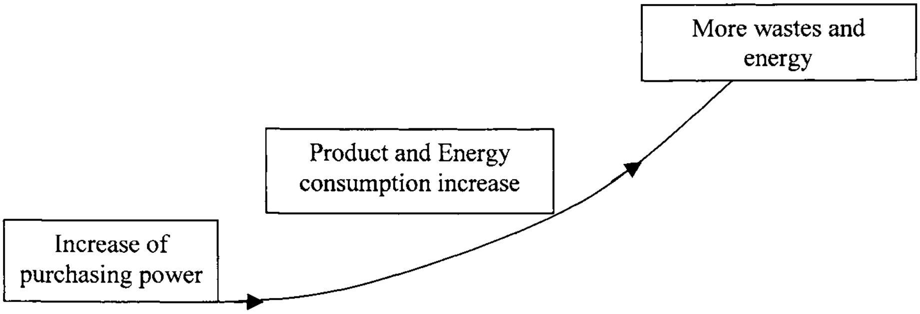

Figure 3. Consequences of the purchasing power increase

One of the main problems with generating garbage in such great amounts is the lack of places adapted for its final disposal. In São Paulo (Brazil), 14,500 tons of garbage is collected daily in the city, in a process that involves 600 vehicles and about 1,850 trips. Five of the existing sanitary depositories in the city are unusable, for a variety of reasons such as saturation. The expectation is that the useful life of the only two depositories in operation is approximately 5 years, considering that each one of them receives five thousand tons of residue daily. The per capita generation of garbage, as well as the population, is increasing and the areas for garbage deposition have not expanded in line with real needs.

Consuming more energy than the generation capacity and producing more garbage than the capacity for appropriate treatment is unsustainable.

Some factors that indicate the need to search for solutions to the problems of garbage generation, mainly in the great urban centers, are :-

A) Shortage of investment in the sanitary sector,

B) Areas for sanitary deposits are close to the urban centers,

C) Growth of the operational costs for collection and final disposition per ton,

D) Gas Emissions.

3. GARBAGE REDUCTION POLICIES AND EFFECTS ON ENERGY CONSUMPTION

We have several types of RSU (Urban Solid Residues). It is known that each type of garbage demands proper treatment, a nominated methodology of Integrated Residues Management (GIR), which looks for the most appropriate way to manage this subject. According to the manual of GIR, elaborated by JARDIM [04], the treatment of RSU can be done according to an *"articulate set of normative, operational and financial actions and planning, that a municipal administration develops based on sanitary, environmental and economic approaches to collect, to treat and to dispose the garbage of its city"* i.e. manage the diversity of types of residues in an integrated way.

Managing the garbage in an integrated way means through a collection system, transport and appropriate treatment, combining types of available solutions and the use of compatible technologies with the local reality, so that the garbage is not the source of problems, in the present and in the future. In the Figure 4, an illustrative diagram is presented, where each block represents an activity taken into consideration by GIR.

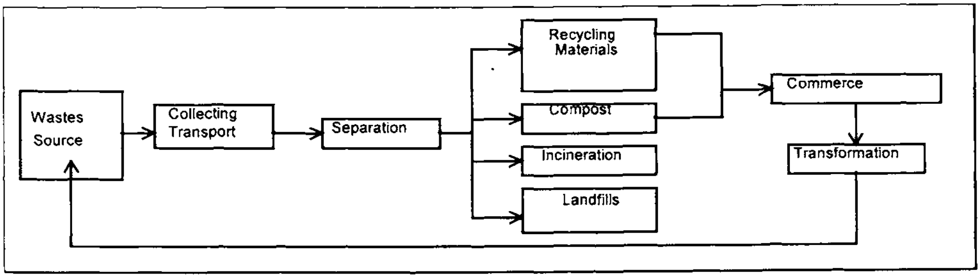

Figure 4. Schematic diagram of Integrated Management of Resources

An important characteristic of GIR that is not always executed in practice is the prioritization of actions, known as the politics of 3 R's, i.e. "Reducing", "Reuse" and "Recycle", before the final disposal. Each "R" obeys a hierarchy. Recovery should not be considered until reduction possibilities are confirmed, nor should recovery be taken into account until reuse has been considered and so on, until arriving at the final disposition (see Figure 5).

Hence, the minimization of RSU seeks:

A. To increase the efficiency in the use of energy and resources;
B. To reduce the generation of residues to the minimum.

To reach these objectives, the following practices are necessary, in decreasing order of minimization of energy resources:

(i) Reduction in the source;
(ii) Recycling of materials;
(iii) Incineration of residues with energy recovery;
(iv) Compost of organic material.

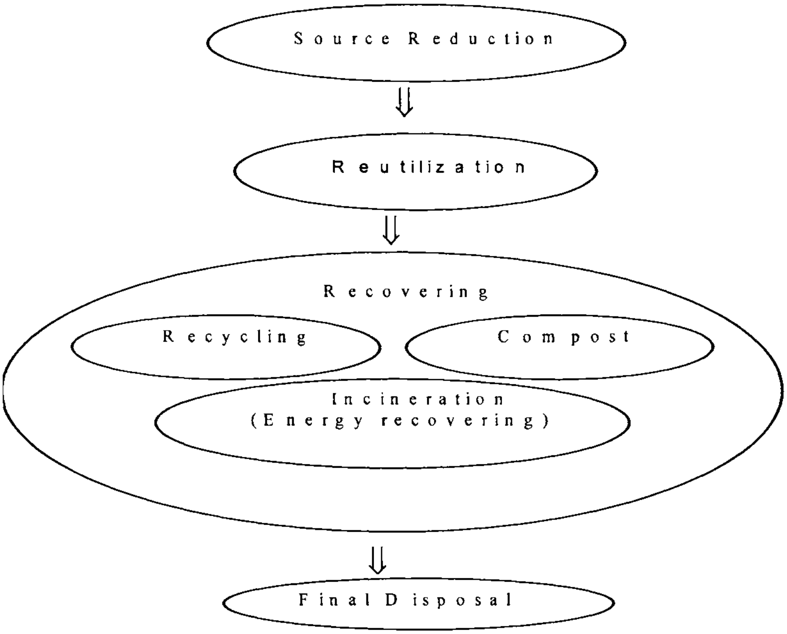

Figure 5. The 3 R's policy.

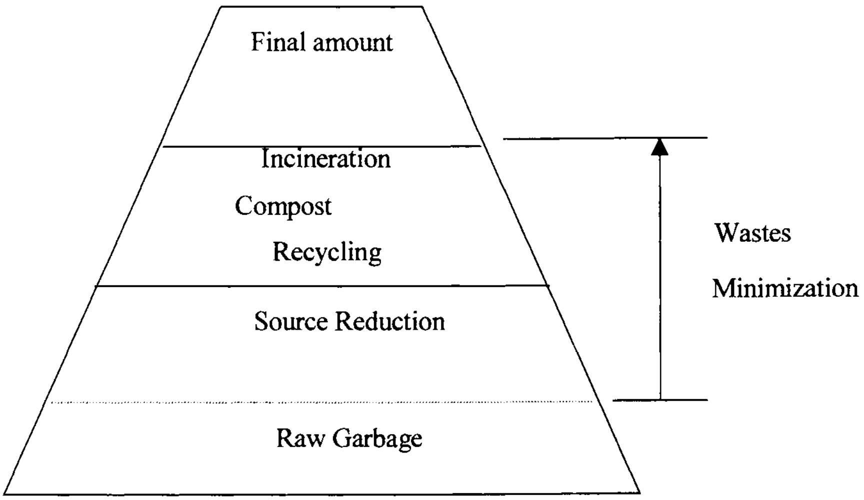

Figure 6. Hierarchy of the waste minimization

Figure 6 illustrates this hierarchy, representing the garbage reduction that can be obtained. In this hierarchy, the first three steps are the measures that contribute most to the problems of shortage of sanitary depositories and that contribute most to the problem of the shortage of energy resources. But, as minimization of residues is efficient, they should be applied together, because separately, each possess a certain inclusion of all types of materials.

Although compost does not represent a significant alternative for the conservation of energy, there is no sense in favoring just the recycling of materials or just the reduction in the source, because of the problem of the sanitary depositories, the measures are complementary. Table 3 illustrates the application of each.

Table 3
Types of materials suitable for the minimization of RSU.

Source Reduction	In practice, restriction in relation to materials does not exist. Even so the easiest products to reduced are, in general, the disposable ones.
Recycling	Recycling is indicated for materials whose scraps can be marketed easily. In decreasing order, the materials recycled with larger value of resale are aluminum, plastics, paper, steel cans and glass.
Incineration	Efficiency of the incineration process is related to the calorific power of the garbage, influenced by the high presence of combustible materials, low humidity and a low amount of inert materials.
Compost	Sweep of public fairs, garbage from restaurants, foods in general and organic materials.

Wastes minimization is a systemic way of reducing the amount of generated garbage and of conserving energy, each approach favours a certain type of material. While recycling can be profitable for materials such as aluminum, paper or glass, incineration is viable for garbage with a high concentration of fuel materials and with a low humidity level. The compost acts with organic materials and the reduction in the source can be applied to most of the materials.

Among the four lines of performance of the minimization of RSU, reduction in the source is the most important. While the reduction in source acts as a preventive measure to the generation of RSU; recycling, incineration and compost act as mitigation measures.

4. WASTES MINIMIZATION AND ELECTRIC ENERGY CONSERVATION

Of the evaluation processes, in the context of the conservation of electric energy, the minimization of RSU can be included in the planning of the electric sector expansion, through a systemic planning, as the Integrated Resources Planning – IRP [07].

IRP, in a simplified way, in accordance with the analysis of the exploration of the minimization of RSU, can be considered as a methodological tool that recognises integral concerns and priorities of the companies, the government, regulatory bodies, consumers, environmentalists and NGO's, whereas the larger concern is with strategic aspects.

If applied in the electric sector, its main characteristics as an advanced form of planning are:

- Analyzing, in a detailed and comparable way, a great number of supply options and of actions on the demand of energy;
- Try to put into account, i.e., to quantify and evaluate the social costs associated with different opinions;
- Motivating public participation;
- Evaluating risks and uncertainties, originated from external and internal factors through to planning and, also, of the current options;
- Seeking consent in the preparation and evaluation of expansion plans of electric energy companies.

IRP can also aid the investment decisions made by the utilities, for example, in the short term, when the utility prefers to acquire energy instead of build new plants.

An incentive for the utilities to apply IRP is the possibility of postponing the costs of energy generation systems in expansion, transmission and distribution. IRP allows optimum achievement which is continuous and monitored in the long and short term. It can be done through programs of energy management, for example, with minimization of environmental impact and with the participation of several sectors of the economy and society.

The methodology of IRP possesses some points that can be complementary to the methodology of the minimization of RSU. For example, where IRP approaches the subject of electric energy supply, the minimization of RSU, through the approach of treatment and final disposition of residues, ends up contributing to energy saving.

Other intersection points also exist, as follow:

- Implementation of RSU minimization, or IRP initially depends on the will to do that;
- There are wide options with associated costs. In the case of IRP, the options are the several existing energy sources, energy conservation and demand side management, in the case of RSU minimization, the options revolve around treatment forms and final disposition of garbage;

- It is difficult to account for social costs associated with each option;
- Community participation and that of the interested parties is very important;

4.1. ELECTRIC ENERGY FROM RECYCLING

Accepting the principle that production with recycled materials requires significantly smaller energy consumption than production from raw material, the current gains of the energy consumption saving are calculated as illustrated in Figure 7.

In Figure 7, the production of 1 ton of aluminum cans from bauxite consumes about 16 MWh of energy, while, if it were produced from recycled aluminum, they would need just 0.8 MWh of energy. Thus, the production of a new can of aluminum starting from a recovered one saves 95% of energy. In the production of 1 ton of steel bars, the utilization of scrap consumes about 1.8 MWh of energy, while the production starting from iron raw material consumes about 6.8 MWh, that is to say, 74% less energy. For paper, the energy saving is 71% and, in the case of glass about 13%, since the melting point of reused glass is between 1,000 to 1,200 ^{O}C, whereas the melting point of glass from raw materials is between 1,500 and 1,600 ^{O}C.

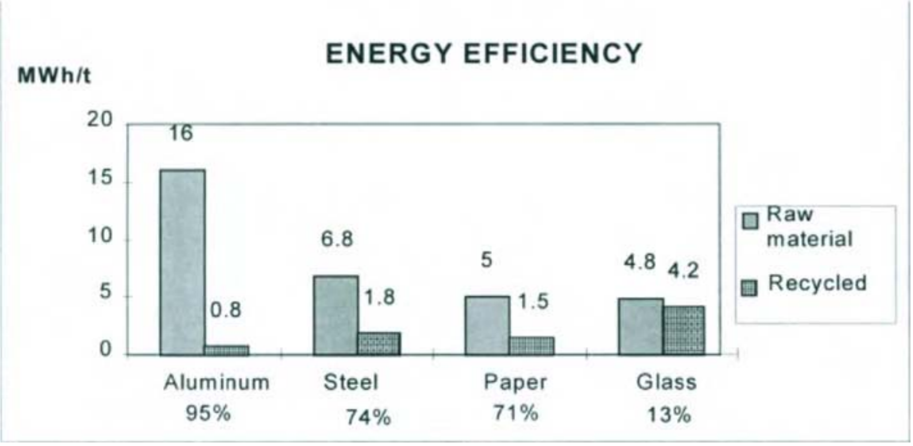

Figure 7. Energy efficiency through the use of raw material or recycled material.
SOURCE: Reference [01]

4.2. ENERGY CONSERVATION FROM INCINERATION

We have direct and indirect forms of exploitation of the energy present in the garbage. The traditional way of direct energy recovery from the garbage is through incineration. Other methods also exist, like the collection of methane gas through anaerobic decomposition.

Incineration is the combustion of garbage in special ovens, using oxygen, turbulence and continuous temperature control. At the end of the process, there is a significant reduction in the weight and volume of the incinerated garbage.

It is possible to obtain energy from residues through incineration, in the case of residues which are combustible and without excessive humidity. The heat produced can be used for direct heating in vaporization processes or to generate electricity. Some liquid residues can also be used in addition to conventional fuels.

The incineration plants use furnaces to burn residues, heating up water that passes through pipes, to be used in other processes. In this system, even dangerous residues can be used. Large scale plants burn from 500 to 1000 tons of residue per day, while smaller plants burn between 50 to 100 tons of residues per day. Very large plants allow the advantage of economy of scale, in the use of the residues and in the generation of energy, as the vapor turbines used can be larger and therefore more efficient. Plants of reduced scale are useful where the number of inhabitants in a community are between 30,000 and 200,000, producing between 50 and 200 t/day of urban solid residues. They have the flexibility of adjusting to demand and also of maintenance, by using a rotation system of the plants that allows the planned closure of some plants. The disadvantage is the pressure of the generated vapor, which is usually low.

4.3. ENERGY CONSERVATION FROM WASTE REDUCTION

Gilnreiner [03], proposed a methodology based on 3 variables to be considered in the probability of success of reduction in the source programs of RSU.

The first variable, nominated EFFECTIVENESS, or success probability, was characterized mathematically as the following expression:

$$\text{EFFECTIVENESS} = \text{POTENTIAL} \times \text{ACCEPTANCE} \qquad (1)$$

Where POTENTIAL is the recoverable portion of RSU in percent or by weight. The ACCEPTANCE is the proportion of that accepted and the rejection of the strategies adopted for the reduction in the source.

While the POTENTIAL is related to the composition of materials contained in RSU, the ACCEPTANCE depends on the human factor.

The ACCEPTANCE can be stimulated through taxing or campaigns to gain understanding and awareness. For example, in Bonn, Germany, the government instituted a tax on the amount of waste produced per residence. In that way, the inhabitant pays for the garbage that is produced, stimulating the generation of less garbage.

Based on the methodology of Gilnreiner [03], the following expression is proposed to determine the energy saving potential due to reduction measures in the source:

$$E_C = Q \times E_P \times \text{POTENTIAL} \times \text{ACCEPTANCE} \qquad (2)$$

Where:

E_C = Conserved energy due to reduction of the garbage generation at source. In this case, all the types of energy used in the production chain (for example, diesel, alcohol, coal, and

electricity) should have its units converted for a unit of reference (for example Wh, joule, cal/h or tep)
Q = Equivalent amount of certain material or discarded product, in weight
E_P = Equivalent saved energy for each 1 ton of a certain material

5. FINAL CONSIDERATIONS

The minimization of residues is in general referenced for the Industry to characterize a series of practices that seek the reduction of costs through the efficient use of the material resources involved in its productive processes. The examples of these practices are, the reduction of leftovers or defective pieces, the recovered refuse, revision of production procedures and an improvement of managerial practices.

The appearance of environmental norms applied to industry, as the series ISO 14000, illustrates the importance of practices of prevention of environmental accidents and of the minimization of residues, mainly because these practices translate into competitive advantages in the market.

In this work, the concept of the minimization of residues by industry benefits the approach to other residue types, that is garbage generated by urban centers, also called urban solid residues (RSU).

While for the Industry, the minimization of residues translates into competitive advantages in the market, the minimization of urban solid residues can be translated into advantages for society, because it contributes to the conservation of resources, including raw materials, water and energy, in agreement with the principle of a sustainable development and contributing to the preservation of the environment.

The minimization of urban solid residues includes, the use of organic residues compost, materials recycling, residue incineration and a reduction at source. However, to-date none of these techniques have been fully developed. It is considered that in Brazil less than 1% of all urban garbage collected gets any kind of treatment. Among them, the recycling of materials is the most popular. Campaigns promoted by the industries that survive on recycled materials, paper, plastic, glass, aluminum and steel reach the consumers daily through television, posters and the labels of its products. Commercial interests stimulate the consumption of recycled materials, in spite of not all materials being totally recycled.

Even so, the recyclable materials are not the only types of residues that fill the sanitary depositories. Recycling cannot be seen as the single solution for sanitary problems of urban centers.

The *Agenda 21* is clear in relation to the need for the revision of consumption patterns, mainly with that of disposable materials. Today, however, the consumption of disposable products is encouraged and often sold as clean products (or environmentally healthy), for the simple fact that they are recycled. Actually, as the system of selective collection is still not very meaningful, nor every material able to be recycled is recycled, this results in final disposal in the sanitary depositories.

It is clear that the proposed themes are related and address sustainable development, offering a more direct impact to the solution of the problems of capacity exhaustion, of adequate treatment of RSU and the need for energy conservation.

It is important to point out that the challenge here, although not giving ready solutions to such problems, forms an indicative base that can be built upon. From this base, studies and more specific research can be focused and certainly should be done.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Use of waste generated by shoe counter scrap pieces in plaster of Paris composites

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The growing increase of industrial waste of difficult degradation is a major concern for industries due to environmental concerns and the strong action of environmental organizations. The 'Centro Tecnológico do Couro, Calçados e Afins' (CTCCA), in cooperation with a group of shoe companies, proposed a research project to the University Vale do Rio dos Sinos aiming at recycling counter scrap waste generated by shoe industries. The present paper describes the investigation undertaken by a research team at UNISINOS to develop a competitive alternative for recycling this waste material.

In this study a new composite material combining plaster of Paris (gypsum) and waste ground in a knife mill was used. The different types and amount of waste materials available for recycling were studied to select the most suitable. This was followed by a thorough chemical and physical characterization.

This work presents the mechanical properties of composites molded with plaster of Paris and counter scrap pieces, determined by compression, impact and flexure strength tests. Results so far indicate that the recycling of these materials in the production of a new construction material is a sound alternative. It was found that some admixtures significantly improve impact resistance properties. Additional characterization studies of these composites are currently under way, alongside with the determination of thermal, acoustic, and durability properties.

1. INTRODUCTION

The reduction in environmental pollution has been the focus of attention of the Brazilian government environmental protection offices, which have set limits for atmospheric emissions and the treatment of liquid waste, as well as regulations for the disposal and classification of waste in landfill sites. The option left to waste-generating industries is the reduction in waste levels produced. This can be effected by improvements in their manufacturing process, the reuse of materials and recycling schemes.

This paper presents the research project currently under way by a team of UNISINOS researchers on the production of a new material for the civil construction sector by recycling shoe counter scrap. The counter is one of the components used in the manufacture of shoes. It lends the shoe structural support and shapes the heel and toe box. It is produced by impregnating sheets with ethylene-vinyl-acetate (EVA) based resins. The resulting sheets are stored in rolls and are then cut in plates. The counter piece is cut out from these plates using cutting dies. The counter is cut in different shapes according to the shoe model being manufactured. When the counters are cut out from the plates, a 'skeleton' of material results, i.e. the scrap material. The counter piece manufacturing process generates from 13% to 25% of waste material by weight depending on the shape and model of counter piece produced. Estimates for total amount of counter scrap generated in this area run at 80 metric tons monthly. According to manufacturers, currently available technology and costs do not make the industrial reuse of this material feasible.

The new material is obtained from the addition of shoe counter scrap which is cut in a knife mill to calcium sulfate hemihydrate matrixes (plaster of Paris). This research started from the hypothesis that it is possible to produce a composite where scrap is added to plaster of Paris paste and produces a high-performance composite. It is believed that the scrap will behave like a fiber thus improving some mechanical properties of the composite and producing changes in its thermal and acoustic properties.

This study is focussed on the characterization of chemical, mechanical and physical properties of the scrap material used as well as microstructure studies to assess its application to the civil construction sector. Tests were run to determine tensile strength, water absorption, specific and unitary gravity for different particle sizes, as well as a structural analysis using an electron microscope.

The use of waste as materials and components for the civil construction sector seems to be a sound alternative, with outstanding benefits to society, namely, the reduction in the use of natural raw materials, the reduction in the power used in producing new materials and the drop in pollutant emissions.

In order to set up a successful recycling scheme involving two diverse industrial sectors, it is essential that integration mechanisms be established between the waste-generating industry, the recycling technology developer and the future users of this technology. The whole process must be supported by a scientific approach to research, which is essential to warrant the success of this enterprise.

Figure 1. Scrap material generated by sheet cutting.

2. MATERIALS

2.1 Binders

Chemical and physical tests were performed to characterize the materials. This allowed the selection of the most suitable types of counter scrap and gypsum to be used in the project.

The gypsum matrix used calcium sulfate hemihydrate with slow hardening to allow more time for the mixing, molding and setting of the composite. The gypsum comes from the state of Pernambuco (Brazil), hardening onset starts after 22 minutes and it is over after 35 minutes.

2.2 Scrap

Counter pieces are produced by impregnating sheets (CTI) or laminating non-woven Bidim sheets (CTL) with EVA-based resins. The two kinds of scrap materials are classified under the Brazilian Standard NBR 10004 as "class II waste – non-inert material". The main difference between the two minerals lies in the type of substrate.

The tensile strength of the counter is anisotropic and ranges from 9.3MPa to 24MPa. Water absorption is lower than 3% on average for the laminated counter and ranges from 40 to 60% for the impregnated material. After the scrap has been ground, however, these values rise significantly and depend on the particle size obtained. Specific gravity for laminated counter pieces ranges from 0.4 to 0.7g/cm^3.

Figures 2 and 3 show the two types of sheets.

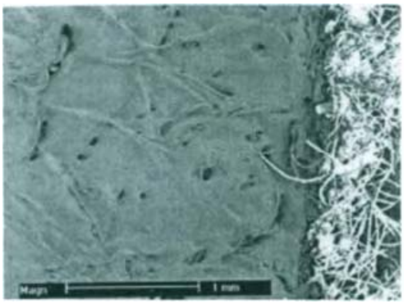


Figure 2. Microscope image of the laminated counter scrap.

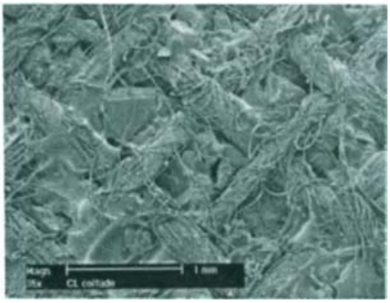


Figure 3. Microscope image of the impregnated counter scrap.

It can be seen that the microstructure of the thermoplastic counter plate is made up by a non-woven sheet with fibers arranged at random and impregnated in synthetic resins. The surface shows non-oriented fibers imbedded in the resin, which forms a continuous film. After grinding, the counter displays a large number of non-oriented fibers due to the maceration of the impregnating resin which no longer forms a continuous film, and the original structure of the material is completely changed.

The laminated thermoplastic counter shown in Figure 3 is made up by a resin-free fabric. The fabric pattern can be easily identified as it is made up by interlaced threads (twisted fibers). In this case, most laminating resin is located in the gaps between the threads. After grinding there is a loss of orientation of the fibers that make up the fabric.

3. ASSESSMENT OF THE CONCENTRATION AND CHARACTERIZATION OF COMPOSITES

3.1. Preliminary Studies

The scrap material used consisted of impregnated and laminated thermoplastic counter scrap which was ground in a knife mill in two different particle sizes with fineness modulus from 4.3 to 5.9.

Different admixtures and concentrations of scrap were studied in relation to the characteristics of the fresh mortar and its resulting composite. The composites were molded with scrap concentrations ranging from 10% to 25% of ground scrap by weight in the gypsum matrix. The mixing was effected in a vertical axle concrete mixer. A specific methodology was developed to guide the mixture of materials.

In this way, the following items were identified: **a)** ideal mixing sequence: it was found that the best sequence of addition is to first mix the water and the ground scrap for 1 minute using a mechanical mixer and only then add the gypsum, with mixing continuing for 2 more minutes; **b)** waste concentrations used: the mix workability is adversely affected for scrap concentrations above 25%; **c)** particle size distribution of the scrap addition: larger particle sizes (FM=5.9), in both wastes make mixing and molding procedures difficult; **d)** removing the specimens from molds: the molds have a base with adjustable side plates and aluminum cornerpieces. The mold is greased with vegetable oil and specimen removal from the mold is easy after a 45-minute curing time; **e)** surface finish in the hardened state: composites with up to 10% concentrations of small particle size counter scrap display smooth finish. As concentrations and/or particle sizes increase, the specimen surface becomes rough.

For each admixture used, test specimens were molded to determine mechanical properties. The gypsum composites were tested for compressive strength, flexural strength and impact resistance.

4. MECHANICAL CHARACTERIZATION TESTS

Compressive strength, flexural strength and impact resistance tests were run to study the mechanical properties of the composite.

To make comparison between specimens possible and to analyze their behavior, the samples were all molded according to the same mixing, curing and removal from mold procedures.

4.1 Compressive Strength

Compressive strength values for the composites were determined as a function of the strength of cubic test specimens (5x5x5cm). Three specimens were molded for each variable tested, and mean results are shown in Figure 4. The influence of the following variables was analyzed in this test: scrap concentrations (0%, 10%, 15% and 20%); type of scrap waste used (impregnated or laminated counter scrap); setting process (manual and mechanical).

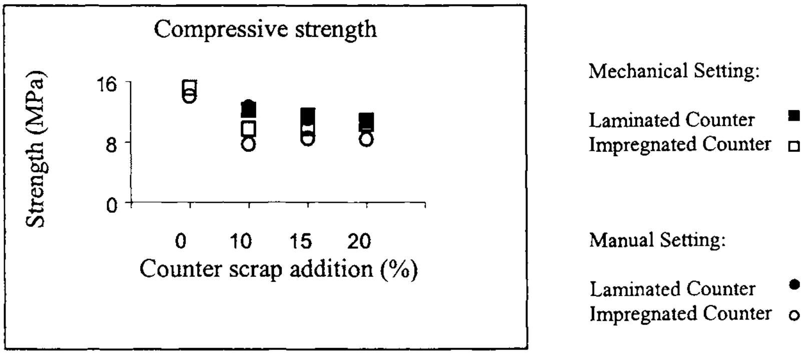


Figure 4. Mean Compressive Strength Values for Test Specimens cured by 14 days with and without the Addition of Laminated and Impregnated Counter Scrap. Water/gypsum = 0.57 .

4.1.1 Considerations on the results

Results obtained indicate that the variables studied have an effect on the compressive strength properties of the composite.

The type of counter scrap added causes different test behaviors to appear. The series of test specimens with the addition of laminated thermoplastic counter scrap exhibit higher strength than those with the addition of impregnated counter scrap. The series of test specimens prepared with mechanical setting displayed higher compressive strength values than those prepared manually.

As expected, the addition of counter scrap caused a reduction in the compressive strength values of the matrix. This indicates that the composite behaves like fibrous materials as far as compressive strength is concerned, since the latter exhibits poorer compressive strength when compared to that of the reference mortar due to the increased porosity of the composite (AGOPYAN, 1991).

4.2 Impact Resistance

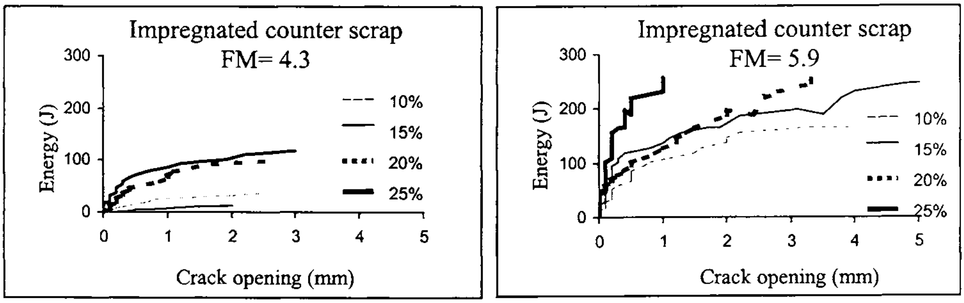
The test method used was developed from the Standard Project 2:02.10.084 of the Brazilian Association of Technical Standards (ABNT) and JIS 6745. The test consists of assessing the impact resistance of a test specimen that is submitted to successive drop cycles of a steel sphere, and the specimen is checked for cracks. The test specimens used in the test are rectangular plates measuring 20 x 30 cm and 2-cm thickness. The energy value of the successive impacts is determined with equation 1:

$$E = \Sigma (m\, g\, h_i), \qquad (1)$$

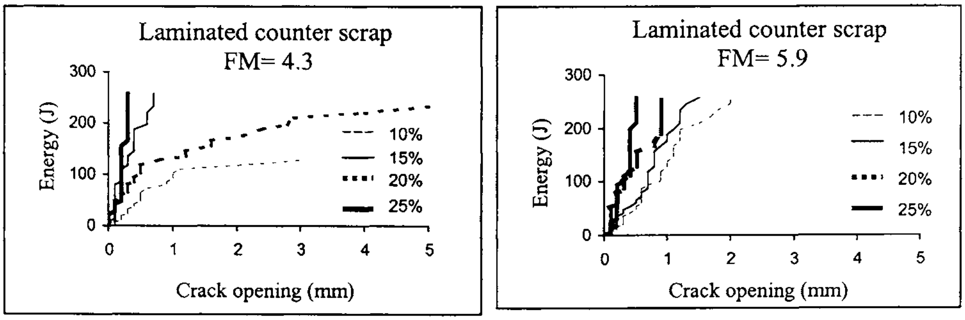
Where:
E = resulting impact energy after "n" cycles (joules);
m = mass of a metallic sphere used for the impact (m = 623g);
g = gravity acceleration ($g = 9.8\ m/s^2$);
h_i = drop height at each impact.

A preliminary study was first performed using four sets of test specimens with scrap concentrations of 10, 15, 20 and 25% in order to assess the composite behavior in this test.

Two of the test specimen sets were prepared with impregnated counter scrap, one with a 4.3 fineness modulus (FM) and the other with a 5.9 fineness modulus. The other sets were prepared with laminated counter scrap. A series of three control specimen tests, with no addition of counter scrap, was prepared. Test results are shown in Figures 5 and 6. Results for control test specimens are not shown in any figure because the test specimens burst in the first drop of the sphere.



Figures 5a and 5b. Impact resistance of test specimens with different ground impregnated counter scrap with a 4.3 and 5.9 fineness modulus, respectively.



Figures 6a and 6b. Impact resistance of test specimens with different ground laminated counter scrap with a 4.3 and 5.9 fineness modulus, respectively.

These preliminary studies showed the different behavior of test specimens molded with gypsum paste and with the composite. The control gypsum matrix (no scrap added) exhibits sudden burst at an energy level of 0.94 J. The composite was shown to be more ductile with considerable plastic deformation properties. The best performance was observed in the laminated counter scrap composite series, where cracks were found to be limited to a small area. The behavior of composites improves as the concentration of scarp increases. Test specimens with large particle size scrap have a better performance.

Series of three test specimens with scrap concentrations of 20% and 25% were prepared. Low fineness modulus scrap (FM= 4.3) was chosen because of the workability desired in the fresh composite.

Figure 7 shows the mean results for the three test specimens in each series tested according to two criteria: **a)** behavior of test specimens throughout the tests. The test is over when the test specimen fails or when the accumulated energy reaches 227.37J, a value equivalent to a 200-cm drop of the sphere (figure a); **b)** energy level to produce a crack (figure b);

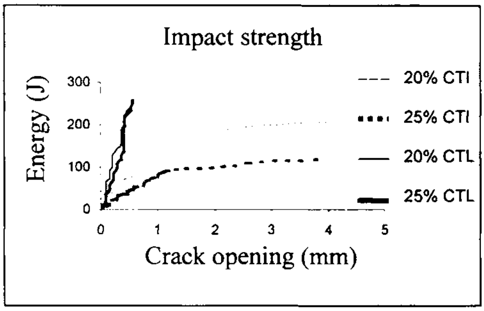


Figure 7a. Mean behavior of the series with added laminated and impregnated thermoplastic counter scrap (CTI e CTL).

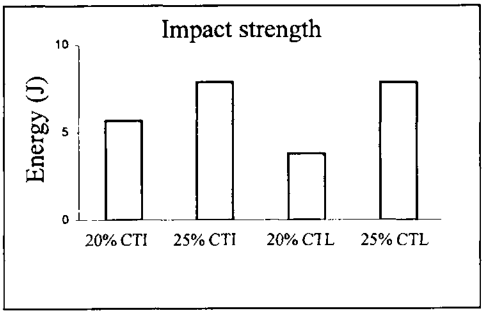


Figure 7b. Energy needed to produce a crack.

4.2.1 Considerations on the results

Figure 7a shows that test specimens with the addition of laminated thermoplastic counter scrap show better impact resistance with more delimited cracks. Series with the addition of impregnated thermoplastic counter scrap show increased crack diffusion, particularly in those test specimen series with lower concentrations of scrap. It can be observed in Figure 7b that the series of test specimens with a concentration of 20% of laminated and impregnated thermoplastic counter scrap is the ones with the first crack.

This difference in behavior of the test specimens associated with the type of scrap added can be explain by the difference in the materials themselves, namely the structural material used in each type of counter. Counters produced with a fabric substrate (the laminated counter in this case) display better mechanical properties than the counters that are manufactured with a non-woven sheet (impregnated counter) (SHERER, 1994).

Results confirm the assumption that ground counter scrap lends fiber-like properties to the composite. Impact resistance is one of the properties that show greater improvement with the use of fibers, their greatest benefit being the changes in the behavior of the material after the onset of cracks. Cracks are more delimited (reduced diffusion) and the material shows improved ductility (AGOPYAN, 1991; JOHN and others, 1997).

4.3 Flexural Strength

The flexural strength in the composites was tested according to the ASTM C78-94 test method. Test specimens measuring 25cm x 5cm and 2.5-cm thick were used to check whether there are improvements in the elastic properties of the composite and establish the relationship between stress and creep deflection on constant load. Test specimens used in this test were prepared under the same conditions described in the impact strength test: three series of test specimens with water/gypsum ratio = 0.57, the addition of ground counter scrap with fineness modulus = 4.3 in 20% and 25% concentrations. Mean results for each test specimen series are shown in Figure 8.

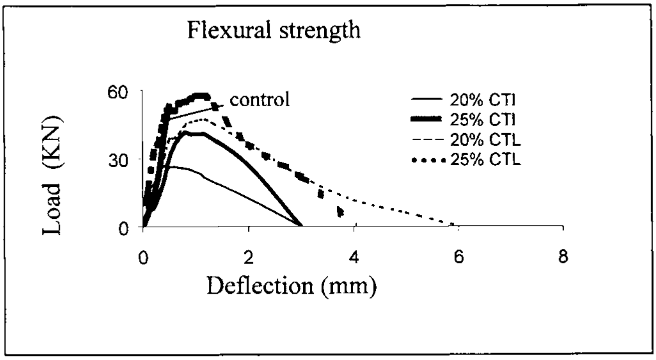


Figure 8. Mean behavior of the series with added laminated and impregnated thermoplastic counter scrap (CTI e CTL).

4.3.1 Considerations on the results

It can be seen here that the properties tested display a similar behavior to those found in the impact resistance test. It was observed that the series of control test specimens can withstand a load of 60Kgf with a sudden failure and no creep deflection whereas the series with the addition of counter scrap show considerable creep deflection with no failure. The series of test specimens molded with the addition of laminated counter scrap show higher load and creep resistance when compared to those prepared with impregnated counter scrap.

5. FINAL CONSIDERATIONS

The mechanical characterization test results presented in this study indicate that the use of this scrap in a gypsum matrix improves some properties, particularly impact resistance and flexural behavior pointing at a promising composite for use in civil construction applications and offering a recycling alternative for this industrial waste.

Additional characterization studies of these composites are currently under way, alongside with the determination of thermal, acoustic, and durability properties.

After characterization tests still in progress are completed, further studies will be developed into production costs and the identification of a civil construction material with a good marketing potential. The actual results show that it might be used as a wall component. Once the type of material to be produced has been defined, prototype specimens will be molded to study its performance, and these results will be used to justify its marketing.

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Waste Materials in Construction
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Testing of soil and inorganic residues prior to utilisation: Development of rational limit values and adaptation of test methods

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This paper describes a methodology for regulatory testing and evaluation of the environmental properties of soil and inorganic waste materials prior to utilisation. The methodology establishes a direct relationship between the risk posed to the groundwater by various utilisation scenarios for soil and granular mineral waste materials and the results of leaching tests performed on the waste. The concept is based on flux considerations and does not take attenuation mechanisms into consideration. Only impacts on the groundwater quality are considered in this model, and it must be supplemented with other relevant criteria. The application of the model is demonstrated for two utilisation scenarios with coal fly ash. Leaching data, which can be used as input to the model, are scarcer for soil than for waste materials. As part of the pursuit of soil leaching data, the paper also discusses how a batch leaching test developed for testing of granular mineral waste materials can be adjusted and applied to soil/contaminated soil. Among the recommended adjustments is to use a 0.001 M $CaCl_2$ solution rather than pure demineralised water as the leachant, as this will prevent clogging of the filters with fine materials. It is further recommended always to use a contact time of 24 hours, since this is practical and appears to increase reproducibility compared to short contact times.

1. INTRODUCTION

Large amounts of inorganic residual waste materials (e.g. construction debris and building rubble, bottom ash from MSW incinerators and coal-fired power plants, steel slags and other industrial by-products) and lightly contaminated soil are produced in most European countries. Due to the increasing scarcity of many virgin raw materials and the limited space available for landfilling, there is a substantial initiative to utilise rather than landfill these alternative raw materials. The interest in utilisation of waste materials, however, often collides with the intentions to prevent or limit potential impacts on the environment caused by the leaching and subsequent migration of contaminants from the utilised waste materials. Therefore, utilisation is often subject to regulations, which require the waste products to be characterised and meet specific criteria, if permission for utilisation is to be granted.

The characterisation required is generally based on analysis of the total or partial content of selected contaminants and/or on the performance of a specific leaching test. The criteria to be met are normally expressed as limit values, which must not be exceeded by the test results. In terms of risk assessment, the total or partial content of contaminants may primarily be related to the human contact or ingestion pathway and exposure, whereas the leachability may be related to the potential risk of release and migration of contaminants, which may subsequently reach and contaminate groundwater (drinking water) or surface water bodies, or they may contaminate the soil through which the leachate is passing.

From an administrative point of view, waste/soil utilisation regulations based on tests and limit values appear to be a satisfactory management tool. From a scientific and environmental perspective, however, the situation is often less satisfying because of the general lack of relationship between the actual risk of an environmental or a health impact and the limit values. This is due to the pragmatic way in which limit values are often established, and it is particularly pronounced in those cases where the total or partial content of contaminants is used as the only criterion for whether or not a waste material or a soil may be utilised.

This paper will focus on two aspects of testing and utilisation of soil and inorganic waste materials. Firstly, a concept and a methodology, which allow the setting of risk-related limit values for testing the leachability of waste/soil to be utilised, will be presented. In principle, there is no difference between the evaluation of waste materials and soil in this system. There are, however, some fundamental differences between the properties and the leaching behaviour of inorganic waste materials in general and soils. These differences must be reflected by the applied test methods, most of which were originally developed for testing of waste materials. The second part of this paper discusses some of the problems involved in the testing of the leachability of soils and of adapting leaching tests developed for granular waste materials to soil testing.

The concepts and methods described in this paper were partly funded by the Danish Environmental Protection Agency, DEPA (Hjelmar et al. 1996, 1998 and 1999), but the opinions expressed are those of the authors and no official endorsement from DEPA should be inferred.

2. A NEW RISK ASSESSMENT MODEL

2.1 Methodology

The methodology presented here establishes a relationship between the result of a leaching test carried out on a soil or a granular waste product and the environmental risk posed by a particular civil engineering utilisation application scenario of that soil/waste product to downstream groundwater. Only the potential impact on the groundwater quality in terms of elevation of the concentration(s) of one or several leached contaminant(s) in the groundwater at a downstream point of extraction for drinking water purposes is considered. However, the model may be generalised to include the potential impact on surface water bodies as well (Hjelmar et al. 1997). The methodology allows the setting of limit values to be divided into two parts: a series of practically objective calculations and a few decisions based on environmental policy. In the case considered, the policy decisions consist of setting maximum allowable values of the increases of the concentrations of various contaminants in the groundwater at the point of extraction (at the well). The more objective calculations consist of using a series of connected scenarios to establish a relationship, firstly between the result of a leaching test and the potential flux of contaminants out of the utilised material, secondly between the flux of contaminants and the elevation of the contaminant level in the groundwater.

2.2 The physical scenario

The soil or the (inorganic) granular waste product which utilised e.g. as a filling material in an embankment or a road ramp is described in a simplified manner as a box with surface area A (m^2), height H (m) and bulk dry density d (t/m^3). The material is placed on or below the surface of the ground above an aquifer. The general annual rate of infiltration of precipitation in the geographic area is I (m). See Figure 1. The maximum acceptable concentration (C_V) of a given component in the leachate which appears at the bottom of the box as a result of the percolation of infiltrated precipitation through the material is defined as follows:

$$C_V = GE \times D \times P \times IR$$

where

GE is the maximum acceptable elevation of the concentration of the contaminant in question in the groundwater from the aquifer below the site at the point of extraction;

D is the ratio between the surface area of the groundwater catchment area considered and the surface area of the utilised material or, alternatively, a dilution factor indicating how many times the leachate from the utilised material is diluted from the point of entry into the groundwater to the downstream point of extraction of drinking water from the aquifer;

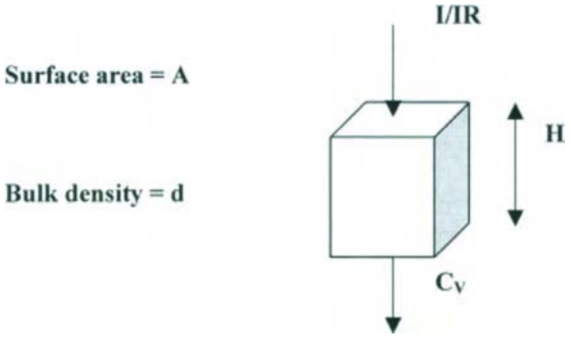

Figure 1
Simplified physical description of a utilisation application containing a granular inorganic material.

P is a priority factor which provides the option of placing higher priority on some aquifers than others, e.g. based on its value as a drinking water resource;

IR is an infiltration reduction factor, which expresses the ratio between the general rate of infiltration, I, in the geographical area in question and the rate of infiltration into (or percolation through) the utilised material which may be reduced by a top cover (increased surface run-off, increased evapotranspiration). The amount of water percolating through the material will thus be I/IR.

This simplified model does not directly take into account the biogeochemical processes in the unsaturated zone below the site and in the aquifer, which would delay and retain a given leachate component during the transport of the leachate from the bottom of the "box" of utilised material to the drinking water extraction point. These attenuation processes therefore constitute an unquantified extra margin of safety.

2.3 The criteria related timeframe, T_C

The leaching of several components, including e.g. salts, from inorganic waste materials and contaminated soil will often show high initial concentrations in the leachate with subsequently decreasing leachate concentrations as the leaching progresses and the liquid to solid ratio (L/S) increases. The concentration of other components (e.g. lead) in the leachate will be controlled mainly by other factors such as pH or redox potential. Since the model is based on the consideration of the flux of contaminants rather than contaminant concentrations, it seems reasonable to use an average value of C_V for a given component over a period of time, T_C, referred to as the criteria related timeframe. This implies e.g. that it is accepted that C_V for the component in question is exceeded during the initial phase of the leaching, whereas the concentration of the component during a later phase will be lower than C_V, ensuring that the average concentration of the component in the leachate over the entire period T_C does not exceed C_V. It will most likely be necessary to assign different values of T_C to different groups of components. Components, which are leached quickly and which are mobile in the unsaturated zone and the aquifer (e.g. several inorganic salts), should be assigned relatively low values of T_C (e.g. 1-3 years), whereas higher values of T_C (e.g. 10 –25 years) can safely be assigned to less mobile components which are leached relatively slowly (e.g. several trace elements). The leaching of certain components, e.g. arsenic, are often solubility controlled in such a way that constantly increasing concentration levels with increasing L/S may be observed for a very long period of time. For such components T_C must be assigned and the model applied with care.

2.4 Specific acceptable mass, M_{SA}, and accumulated leached mass, ALM_C

If the flux of a given component leached from the box of utilised material is considered, the specific acceptable mass of that component per unit weight of utilised material, M_{SA}, (e.g. expressed in mg/kg) which can be leached during the time period T_C may be calculated by substituting the equation defining C_V above into the expression used to calcuate the flux of the component out of the utilised material. This leads to the following equation:

$$M_{SA} \quad = \quad GE \times D \times P \times T_C \times I/(d \times H)$$

The result of a leaching test, which is usually accelerated, may for granular inorganic materials often be expressed as an amount of leached components per unit weight of material as a function of L/S or at a given L/S ratio. Assuming ideal conditions, L/S (e.g. expressed as l/kg = m^3/t) can be related to time for the physical scenario under consideration by the following equation:

$$T \quad = \quad (L/S) \times d \times H/(I/IR)$$

where T is the time corresponding to the value of L/S used. If the same time perspective is applied to the physical scenario describing a utilisation situation for a material and to the interpretation of the result of an accelerated leaching test on the same material, the equation shown above can be used to establish a relationship between the specific acceptable mass, M_{SA}, leached from the utilised material within the criteria related timeframe, T_C, and the result of the leaching test. The impact on the groundwater quality will not exceed an increased concentration corresponding to GE at the point of drinking water extraction as long as M_{SA} is not exceeded. The criteria related value of L/S corresponding to T_C for a given component can be determined from the following equation:

$$(L/S)_C \quad = \quad T_C \times I/(IR \times d \times H)$$

Under idealised conditions where the leached amounts of a given component as a function of L/S based on the results of leaching tests are available and where this description can be assumed to simulate the actual leaching conditions, the following condition must be satisfied to ensure that GE is not exceeded at the point of extraction of drinking water from the aquifer:

$$ALM_{Ci} \quad < \quad M_{SAi}$$

where ALM_{Ci} is the accumulated leached mass of component i found experimentally at the accumulated L/S value $(L/S)_C$ (see Figure 2) and where M_{SAi} is the calculated specific acceptable mass of component i leached from the utilisation scenario.

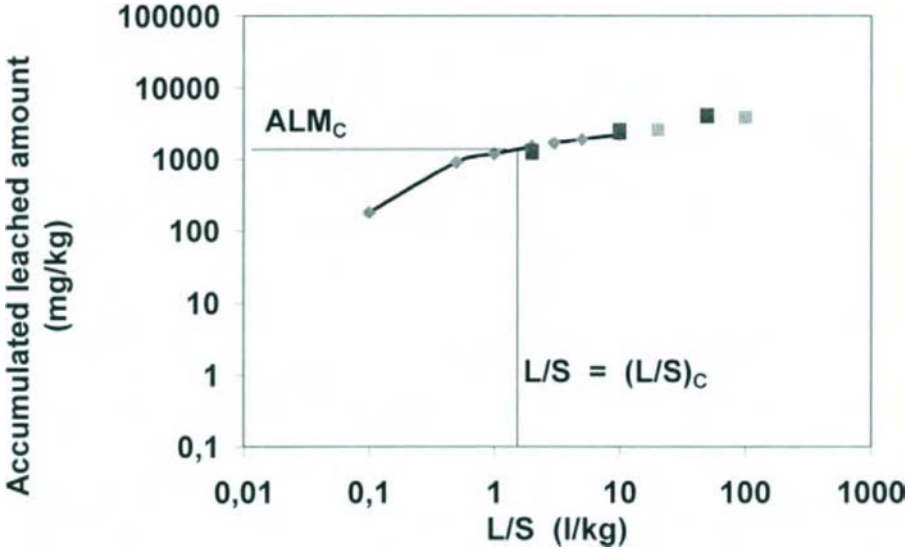

Figure 2
Graphical determination of the criteria related accumulated leached amount, ALM_C.

2.5 Scenario calculations: two examples

To illustrate the use of the concept and the model, they are applied to two different utilsation scenarios: an embankment with soil cover and road utilisation scenario (subbase under a paved road). In both cases the waste material is coal fly ash. The scenarios, which are very simple, are characterised by the parameters shown in Table 1. For both scenarios dilution factors of 10, groundwater priority factors of 1 (high priority), annual precipitation infiltration rates of 300 mm and coal fly ash bulk densities of 1.5 t/m^3 are assumed. It is further assumed that the embankment has an average height of 5 m and a top cover which reduces the rate of infiltration by a factor of 2, whereas the road subbase has a thickness of 0.5 m with a surface pavement which reduces the rate of infiltration by (at least) a factor of 10. The flow regime is assumed to be percolation in both cases.

Two partly leachable components of the coal fly ash, potassium (K) and chromium (Cr), are considered. The relatively abundant and mobile salt ion, K^+, is assigned a criteria related timeframe of $T_C = 3$ years, whereas Cr, which will be moderately mobile as the chromate ion, is assigned a $T_C = 10$ years. The following maximum acceptable elevations of the concentrations in the groundwater at the extraction point, GE_{Max}, are chosen: 150 mg/l (K) and 0.05 mg/l (Cr). The calculated values of the specific acceptable leached amounts, M_{SA}, and the criteria related L/S values, $(L/S)_C$, are shown in Table 2.

In Figure 3, K and Cr leaching results of lysimeter, column and batch tests on a coal fly ash are presented (Hjelmar et al., 1991 and 1997).

From the data in Figure 3, the accumulated leached mass, ALM_C, corresponding to the values of $(L/S)_C$ shown in Table 2 can be determined. The results are presented in Table 3, which also shows the final comparison of ALM_C and M_{SA} for each scenario and each component. The criteria are fulfilled for both scenarios for K ($ALM_C/M_{SA} < 1$) but not for Cr ($ALM_C/M_{SA} > 1$ for both scenarios). If the thickness of the subbase layer in the road scenario is reduced to 0.2 m, ALM_C/M_{SA} values of 0.04 (K) and 0.88 (Cr) are obtained, thus fulfilling the criteria for this scenario.

Table 1
Definition of sample scenarios.

Parameter	**Unit**	**Embankment scenario**	**Road subbase scenario**
Dilution factor, D	none	10	10
Groundwater priority factor, P	none	1	1
Rate of infiltration of precipitation, I	m/year	0.3	0.3
Dry bulk density of coal fly ash, d	t/m^3	1.5	1.5
Infiltration reduction factor, IR	none	2	10
Height of embankment/subbase, H	m	5	0.5

Table 2
Calculation of M_{SA} and $(L/S)_C$.

Scenario	Parameter	Potassium	Chromium
Embankment	M_{SA}	180 mg/kg	0.20 mg/kg
Road subbase	M_{SA}	1800 mg/kg	2.0 mg/kg
Embankment	$(L/S)_C$	0.06 l/kg	0.20 l/kg
Road subbase	$(L/S)_C$	0.12 l/kg	0.40 l/kg

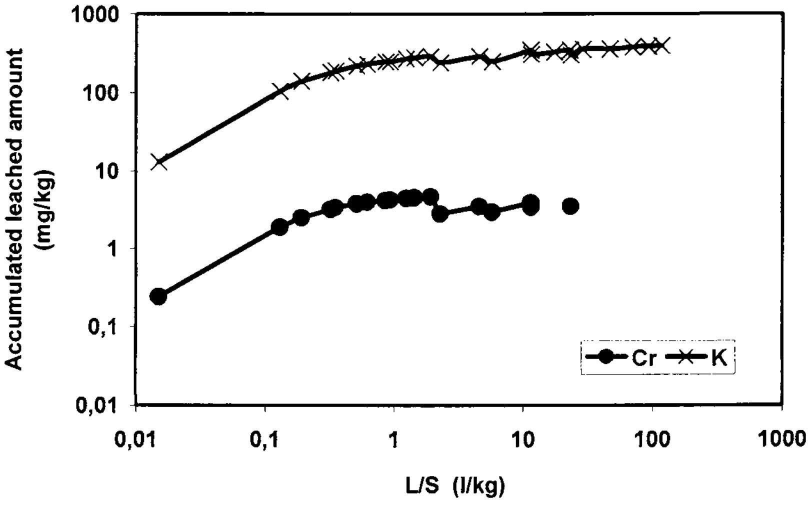

Figure 3
Results of lysimeter, column and batch leaching tests on a coal fly ash covering a range of L/S from 0.015 l/kg to 117.5 l/kg.

From the data in Figure 3, the accumulated leached mass, ALM_C, corresponding to the values of $(L/S)_C$ shown in Table 2 can be determined. The results are presented in Table 3, which also shows the final comparison of ALM_C and M_{SA} for each scenario and each component. The criteria are fulfilled for both scenarios for K ($ALM_C/M_{SA} < 1$) but not for Cr

($ALM_C/M_{SA} > 1$ for both scenarios). If the thickness of the subbase layer in the road scenario is reduced to 0.2 m, ALM_C/M_{SA} values of 0.04 (K) and 0.88 (Cr) are obtained, thus fulfilling the criteria for this scenario.

Table 3
Calculation of ALM_C and check on fulfilment of criteria ($ALM_C/M_{SA} < 1$).

Scenario	**Parameter**	**Potassium**	**Chromium**
Embankment	ALM_C	104 mg/kg	2.5 mg/kg
Road subbase	ALM_C	100 mg/kg	3.6 mg/kg
Embankment	ALM_C/M_{SA}	0.58	13
Road subbase	ALM_C/M_{SA}	0.06	1.8

These results are indicative of the ability of the model to identify leachable components with potentially detrimental effects on downstream groundwater quality. Field observations have actually revealed significantly elevated concentrations of Cr (up to 0.5 mg/l) in groundwater a few hundred metres downstream of a coal fly ash monofill (Hjelmar et al., 1991).

2.6 Other experiences with the model

It is worth noting that the criteria related L/S values needed for the calculations all are relative low (ranging from 0.03 to 0.40 l/kg, see Table 2). This is consistent with the results of several other scenario calculations performed with this method (Hjelmar et al., 1998 and 1999). Often, leaching data are not available for L/S values as low as that. Most regulatory batch leaching tests are performed at L/S values of 10 l/kg or higher. L/S = 2 l/kg is generally considered the lowest L/S value at which it is practically possible to perform a batch leaching test. Most of the regulatory tests currently in use are batch leaching tests, and the use of leaching data from batch tests performed at L/S values higher than those required by the method may lead to ALM_C values that are too high. This may again lead to false failures to comply with the criteria and consequently to rejection of materials and projects which actually meets the criteria for groundwater protection. The solution may be to use column leaching tests (or tests, which can produce simulated pore water) for regulatory (compliance testing) purposes. Normal column leaching procedures can easily produce leachate fractions in the range corresponding to L/S = 0.1 to 0.5 l/kg over a period of a few days to a week or less.

Despite some inconsistencies caused by the dependency of $(L/S)_C$ on the height of utilised material when it is attempted to define limit values corresponding to uncontaminated soil, the concept described in this paper appears promising and useful. The inconsistencies can be overcome using an empirically based convention. The concept has proven a very powerful tool for pinpointing waste materials/soils and utilisation scenarios, which are unfavourable in terms of the potential impact of specifically harmful components on the groundwater quality. It also has the advantage of providing more than one option for improvement of the scenario designs and the waste/soil material properties (both hydraulic design changes and chemical stabilisation changes are e.g. possible). Various general or specific restrictions may be imposed on particular types of utilisation applications of particular types of waste/soil in accordance with the performance of the material and the scenario when the system is applied.

3. TESTING THE LEACHABILITY OF SOILS

3.1 General aspects

There are no fundamental differences between the principles upon which an evaluation of the environmental risk from the release of contaminants from inorganic waste materials and from contaminated soil, is based. In addition, the physical and chemical processes controlling the release of contaminants from the solid phase to the aqueous phase are in most cases the same for inorganic waste materials and soils. The most important of these processes are dissolution/precipitation, complexation, adsorption/desorption, cation exchange, diffusion, and (for some organic contaminants) volatilisation processes. However, when it comes to testing the leachability of contaminants, e.g. inorganic constituents, the basic differences in composition and properties of soil and inorganic waste must be taken in account by the test methods applied.

The basic matrix of many types of inorganic waste consists of one or few major phases, e.g. minerals such as calcite, gypsum, portlandite and iron oxides. The constituents that potentially may be released from the waste are either part of the major phase or mineral (e.g. sulphate in gypsum), contained within these phases (e.g. $CdCO_3$ mineral in calcite) or through surface precipitation or adsorption associated with the surfaces of these main phases or particles comprising the waste. Although the concentrations of some contaminants in some waste materials may be enriched on the surface of particles, often the waste matrix itself is (one of) the contaminant(s).

With the exception of special organic soils with very high contents of organic matter, the principal components of soils also are inorganic. The primary (un-weathered) minerals such as silicates are the main constituents of sandy soils, whereas secondary weathered minerals such as montmorillonite, kaolinite, vermiculite and illite are significant constituents in clay soils. The natural content and occurrence of trace elements are related to the geochemical processes to which the soil has been subjected. The extent and properties of soil contamination is, of course, dependent on the source and on site-specific factors (e.g. texture, soil profile, and water percolation) controlling the spatial distribution of the contaminants in the soil. Generally, the contaminants in soil are found in the secondary minerals or associated with the organic phases and/or the surface of the soil particles, see e.g. Rauret (1997). Thus, it may be difficult to distinguish between trace elements present due to natural processes and trace elements present due to contamination, since almost all trace element are found in background concentrations even in pristine soils. These difficulties are particularly pronounced when the total contents of the inorganic contaminants are considered.

The content of trace elements present in the soil as background concentrations and as more recently added “secondary” contaminants may, however, be easier to distinguish from each other in terms of leachability. The leachability of background elements in soil, which has been exposed to ambient conditions over a long period of time, is likely to be very low, whereas the general leachability of more recently added contaminants is likely to be higher. It is therefore appropriate, both from a risk assessment perspective and from the perspective of detection ability, to develop and use leaching tests to assess the potential environmental impact of contaminated soil.

Most of the existing leaching tests aimed at environmental risk assessment have been developed for inorganic waste materials. It therefore seems obvious to attempt to extend the range of applicability of these leaching procedures to include the testing of the leachability of contaminated soil. In doing this, it is necessary to adjust the existing leaching procedures to account for some of the differences between inorganic waste materials and soil.

Some of the major problems involved in the testing of the leachability of soils and of adapting leaching tests developed for description of the leaching of inorganic contaminants from granular waste materials to soil testing are discussed below.

3.2 Some factors influencing the leaching of soils

Several physical and chemical factors will influence both the total release and the rate of release of potential contaminants. Some of the most important factors are: particle size and homogeneity of the sample, mode of contact between liquid phase and sample material, contact/agitation time, pH (and buffering capacity) in the liquid phase and buffering capacity of the sample material, combined with degree of contact with the atmosphere, redox conditions of the leaching system and the composition of the leachant. In this context, attention will be focused on the role of the composition of the leachant and the contact time.

Other key issues to are to define the background leaching or release of contaminants from soils considered "uncontaminated" and to define safe levels of release as part of the setting of risk-related limit values for testing of the leachability of soil (and waste materials) to be utilised. The latter was discussed in the first part of this paper, and the determination of background levels is addressed below.

3.3 Development of a test protocol: preliminary results

As a part of the investigations of the feasibility of setting leaching based criteria for utilisation of contaminated soil preliminary experimental work was carried out (Hjelmar et al., 1998). For testing of contaminated soil it was decided to use the CEN-proposal for testing of granular waste at compliance level. Procedure C (now prEN 12457-3) was followed. In summary this is a 2-step method (L/S = 2 and 10 l/kg) with contact time of 6 and 18 hours, respectively. The leachant prescribed in the procedure is deionised water. Only leachant from the L/S = 2 l/kg step was analysed as a part of the preliminary investigations. This corresponds to the procedure prEN 12457-1, except that the contact time prescribed in this procedure is 24 hours. The preliminary results are presented and discussed here.

Composition of the leachant

Dionised water is used as the default leachant when the test is applied to granular waste. For testing of soil it is suggested adding an electrolyte to the leachant, since this better than deionised water would simulate soil solution. Testing soil at a liquid to solid L/S ratio of 2 l/kg, which is the approximate minimum L/S at which it is practically possible to use a batch set-up, results in a dilution of the natural pore-water to solid ratio of a factor of 5-10. If the results of the tests are interpreted in terms of release at an accumulated L/S-ratio, the above-presented concept does in principle take this into account. However, there are practical difficulties involved in using deionised water as leachant in testing since the release of contaminants is highly influenced by the ionic strength and the ionic composition of the solution. Using deionised water may thus result in technical difficulties, e.g. problems with separation of the leachant from the soil sample prior to analysis of the leachant. This aspect was further investigated by Hjelmar et al. (1998) who examined filtration (pressure filtration, 0.45 µm particle cut off) time as a function of concentrations of $Ca(NO_3)_2$ and $CaCl_2$ in the leachant. The test was employed with different soil samples according to the test reference given above with the concentrations of calcium nitrate and calcium chloride in the leachant as shown in Table 4.

Table 4
Results of filtration test involving two soil samples.

$Ca(NO_3)_2$ concentration	Filtration time, sec.	
	Pb-sample*	As-sample**
0 M	260	>10000
0.001 M	9	8
0.002 M	7	6
0.005 M	6	5
0.010 M	6	5

*Pb-sample: Pb-contaminated clay-loam soil
**As-sample: As-contaminated sandy soil

Using $CaCl_2$ as alternative to $Ca(NO_3)_2$ gave similar results. In addition, tests on soil samples with a higher content of clay in a 0.001 M $CaCl_2$ solution gave satisfactory filtration results. Based on soil solution studies of contaminated soils, e.g. Holm et al. (1998) and Lorenz et al. (1997) calcium concentrations should be in the range of 40-800 mg Ca/l (0.001-0.002). Since high concentrations of nitrate (due to microbial activity) and chloride (weak complexing agent) is undesired it was decided to use 0.001 M $CaCl_2$ in the preliminary test protocol. Based on the results of these and a number of additional tests it is therefore recommended to use a 0.001 M $CaCl_2$ solution as the leachant when the batch leaching test prEN 12457 is applied to soil samples. When the test is applied to waste materials, the default leachant, demineralised water, should be used.

Contact time

The length of the period of time during which a liquid phase is in contact with a solid phase will influence the quantity of the components leached, unless equilibrium-like conditions are obtained. It is important to set a contact time for the CEN draft batch leaching test, which will be suitable for a variety of contaminated soil types and inorganic waste materials. One of the main reasons is that the contact time needed to reach equilibrium-like conditions may vary substantially between sample types and between components. If the test conditions are very different from the initial conditions of the sample, equilibrium-like conditions may in practice never be reached, e.g. if anaerobic or highly alkaline samples are brought into contact with atmospheric air. Another reason is that from an administrative and operational point of view is it desirable to have test periods that are relatively short and fitted to normal laboratory working hours. Thus, testing periods exceeding 24 hours are often not considered feasible. In order to ensure a maximum robustness of the test, the contact time should be sufficiently long to ensure that the system is close to an equilibrium or steady state condition and that consequently the rate of change of concentration of all components of interest is small or negligible. On the other hand, the contact time should also be sufficiently short to prevent significant test-induced disturbances (e.g. oxidation/reduction, carbonation, bacterial growth) from occurring. From a perspective of planning of laboratory activities, a 24-hour duration of the test will often be optimal.

A preliminary study of the influence of the contact time on the amount of various components leached from soils in the batch leaching test at L/S = 2 l/kg has shown that most major ions appear to approach an equilibrium-like condition within a contact time of 3 to 24 hours and maintain that condition for at least 168 hours. Some of the components which are sensitive to changes in redox potential and/or pH (Al, As, Mn, Fe, Ni and Cd) exhibited substantial differences between the amounts leached when short (less than 24 hours) and longer (more than 48 hours) contact times were used. The redox potential was not monitored, but small pH variations did occur with time after 24 hours and could possibly account for the observed differences between the results of tests with shorter and longer contact times. New tests have been planned to investigate further the influence of the contact time on the test results.

Based on the preliminary results and attempting to balance the advantages and drawbacks of shorter and longer contact times, a contact time of 24 hours is recommended for testing of both soil and waste at L/S = 2 l/kg. This corresponds to the contact time prescribed in prEN 12457-1, and it further appears from yet unpublished results that a contact time of 24 hours leads to a smaller standard deviation than a contact time of 6 hours does.

Background release of contaminants

Figure 4 shows the content of a number of elements in 10 Danish soils, determined after partial digestion with nitric acid at 1 ato for 2 hours (DS 259).

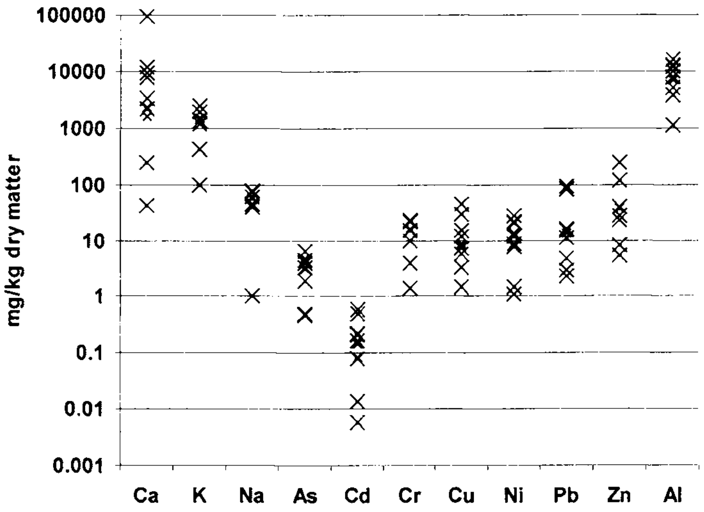

Figure 4
Content of elements in 10 unpolluted Danish soils. Analysed after nitric acid digestion.

The soil samples were collected from rural areas (both agricultural and forest soils) as well as urban areas. Their pH values range from 3.5 to 7.7, and the texture varies from sandy soils to soils containing more than 20 percent (w/w) clay (i.e. particles < 0.002 mm). All the soils were sampled as references or non-polluted soil. However, two of the urban soils exceeded the Danish regulatory limit values for uncontaminated soil for Pb and Cd, probably due to diffuse city-related pollution.

Figure 5 shows the results of the batch leaching test prEN 12457 performed at L/S = 2 l/kg with a 0.001 M $CaCl_2$ solution on the same 10 samples as those presented in Figure 4. The test was performed as step one of the two-stage version of prEN 12457, and therefore the contact time was only 6 hours in this case.

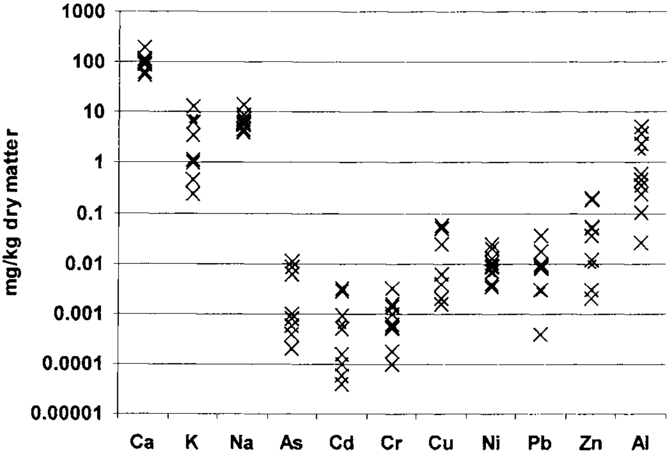

Figure 5
Results of batch leaching tests on 10 unpolluted soils. The tests were performed at L/S = 2 l/kg using a 0.001 M $CaCl_2$ solution.

In Figure 5, the results are presented as ranges representing the leached amounts of the various elements found for each of the 10 samples. In many cases these ranges are of the same relative order of magnitude (1 to 2 decades on a logarithmic scale) as the ranges shown in Figure 3, whereas the absolute amounts leached generally are much lower than those determined by analysis after nitric acid digestion of the soil matrices.

4. CONCLUSIONS

This paper presents a new methodology for establishing a relationship between the result of a leaching test carried out on a soil or a granular waste product and the environmental risk posed by a particular utilisation scenario of that soil/waste product to downstream groundwater. It appears that the major weaknesses of the method, the requirement of leaching data at relatively low L/S values, and some inconsistencies which may occur when potentially uncontaminated soil is tested, can be overcome relatively easily. The model is based on flux considerations and does not take attenuation mechanisms into consideration. Only impacts on the groundwater quality are considered in this model, and it must be supplemented with other relevant criteria to ensure a satisfactory protection of the environment and human health against the potential negative effects of landfilling and utilisation of inorganic mineral waste materials and soils.

The risk assessment methodology is based on the use of leaching tests. Most leaching tests aiming at the assessment of environmental impacts have been developed for inorganic waste materials. A majority of the tests routinely carried out on soils has had other purposes, often related to the agricultural uses of the soil. Therefore, testing of the leachability of soils for environmental risk assessments generally requires some adjustment of existing leaching tests. This paper has dicussed some of the factors influencing the result of a leaching test and some of the technical problems involved in testing the leachability of soils and of adapting leaching tests developed for granular waste materials to soil testing. Based on preliminary experimental results of a batch leaching test at L/S = 2 l/kg applied to soil samples, it is recommended to use a 0.001 M $CaCl_2$ solution rather than pure demineralised water as the leachant, as this will prevent clogging of the filters with fine materials. It is further recommended always to use a contact time of 24 hours, since this is practical and appears to produce more reproducible results. Examples of analyses carried out after nitric acid digestion (partial digestion) and results of leaching tests carried out at L/S = 2 l/kg on 10 expectedly unpolluted Danish soils have been presented. Two of the urban soils exceeded the current limit values (analyses after nitric acid digestion) for soils, which can be utilised without restrictions.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Further development of a process for treatment of APC residues from MSW incinerators

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A process for treatment of semidry and dry APC system residues from MSW incinerators based on an initial aqueous extraction followed by re-suspension and stabilisation of the filter cake with carbon dioxide and/or phosphoric acid was developed in 1994 - 1997 and was shown to produce a material with vastly improved disposal properties. This paper summarises some of the earlier results and presents some preliminary results of a new ongoing R&D project aimed at optimising and preparing the process for full-scale implementation and extending the applicability of the process to include fly ash and wet scrubber sludge. The results of leaching tests performed on residues treated at a new large-scale pilot plant indicate that good results may be obtained for most contaminants using carbon dioxide and phosphoric acid, both for semidry residues and fly ash. Using CO_2 alone also yields good results, but the leachability of Pb is higher at low pH values. Tests also indicate that it may be feasible to use another waste product, namely sewage sludge ash as the source of phosphorous. Further work has been initiated to improve the stabilised residues and reduce the leaching of SO_4^{2-}, Hg and some oxyanions.

1. INTRODUCTION

Solid residues from air pollution control (APC) systems at municipal solid waste (MSW) incinerators constitute a serious and increasing waste management problem in several industrialised countries. The problem of environmentally safe management of these residues, particularly the residues from the semidry and dry acid gas cleaning processes and the fly ash, has not yet been solved in a satisfactory and sustainable manner. The residues are in many cases simply stored indefinitely in big bags or they are landfilled under conditions, which in the long term cannot prevent unacceptable impacts on the environment.

The APC residues, including fly ash, are in many countries as well as in EU legislation classified as hazardous waste due to their high contents of trace elements/heavy metals and soluble salts. Some of the APC residues (those from the dry/semidry lime injection processes) are strongly alkaline due to a substantial content of excess lime, and the high pH favours the leaching of several contaminants, particularly lead. Therefore, treatment is or will be necessary and/or required prior to landfilling (or utilisation) of most APC residues from MSW incinerators.

Substantial efforts have been spent developing treatment processes, which can render these residues more suitable for disposal or even enable beneficial use of the residues. The fact that several of these processes for treatment of dry and semidry APC residues include or are preceded by a washing or extraction step reflects the general acknowledgement that the large content of soluble salts constitutes a major obstacle to the attainment of an environmentally stable treatment product. One treatment process, which resulted in strongly improved environmental properties of the treated residues, was developed and its feasibility proven in a laboratory and pilot scale study, which was started in 1994 and finalised in 1997 (Hjelmar & Birch, 1997; Hjelmar et al. 1997). This paper summarises some of the earlier results and presents some new preliminary results of an ongoing programme for further development of that process.

2. THE RESIDUES

The most common APC system residues from MSW incinerators are those from the so-called dry and semidry lime injection processes and the wet scrubbing process. In some countries the wet and the semidry processes are combined to yield only solid residues.

The residues from the dry and semidry processes consist of a mixture of fly ash, unreacted excess lime and reaction products, primarily calcium chloride, from the acid gas removal system. The material is collected as a fine powder in electrostatic filters or fabric filters. The difference between the dry and the semidry processes are that the lime is injected or sprayed into the flue gas as a powder in the dry process and as a slurry in the semidry process. The dry process is usually somewhat less effective than the semidry process and for the same concentration of acid gases in the flue gas a higher stoichiometric ratio of lime is required to reach the same acid gas removal efficiency as the semidry process would. The residues from the dry process therefore generally have a higher content of excess lime than the residues from the semidry process. Sometimes the fly ash is collected separately upstream of the acid gas cleaning system. In those cases two streams of solid waste are collected: one consisting of fly ash and another consisting of reaction products (mostly soluble salts) and excess lime. The separately collected fly ash typically contains 20 to 25 percent (by weight) of readily soluble salts, mostly chlorides but also sulphates of sodium, potassium and calcium. The admixtures of dry/semidry residue and fly ash typically contain 30 to 35 percent (by weight) of the same soluble salts, but dominated by calcium chloride (or calcium hydroxychloride, CaOHCl, H_2O). With few exceptions, and most notably among these mercury, most of the trace elements/heavy metals present in the residues are mainly associated with the fly ash matrix (Hjelmar, 1993).

In the wet process the fly ash is always pre-collected upstream of the wet scrubber(s). In addition to the fly ash, the process yields a small stream of sludge from treatment of the scrubber effluent and a stream of treated wastewater containing most of the soluble salts. The purpose of the wastewater treatment process is to reduce the content of trace elements/heavy metals in the wastewater to a low level prior do discharge to the sewer or to a recipient. The sludge contains the precipitation agents (often TMT, trimercaptotriazine), trace elements/heavy metals, gypsum, carbonates, hydroxides and other salts. Gypsum is sometimes collected in a separate stream. In some cases, the wastewater treatment sludge is mixed with the fly ash prior to landfilling.

The leachability of some of the components from the fly ash, the dry/semidry residues (with fly ash included) and one example of wet scrubber sludge mixed with fly ash is illustrated in Table 1. The data are results of accelerated laboratory leaching tests carried out as combined column and batch leaching tests (first a column test representing a liquid to solid ratio (L/S) of 0-2 l/kg, then the material was removed from the columns and subjected to a serial batch test representing L/S = 2-5 l/kg and 5-25 l/kg). The table shows that the leachability of salts and most of the trace elements is highest from the dry semidry residues and the fly ash and substantially lower from the mixture of wet scrubber sludge and fly ash.

Table 1
Amounts of selected compounds (in mg/kg) leached from APC residues from MSW incinerators in combined column and batch leaching tests at an accumulated L/S = 25 l/kg. TDS = total dissolved solids. NVOC = non-volatile organic carbon. After (Hjelmar, 1993).

COMPONENT	FLY ASH	DRY/SEMIDRY RESIDUES	WET SCRUBBER SLUDGE + FLY ASH
TDS	210,000 – 230,000	290,000 – 380,000	140,00000
Ca	9,100 – 24,000	61,000 – 109,000	17,000
Na	23,000 – 30,000	12,000 – 17,000	21,000
K	28,000 – 50,000	17,000 – 29,000	21,000
Cl^-	89,000 – 106,000	116,000 – 200,000	56,000
SO_4^{2-}	13,000 – 41,000	470 – 3100	32,000
As	0.10 – 0.19	< 0.02 – 0.04	0.28
Cd	0.051 – 35	0.03 – 0.44	< 0.0006
Cr	0,053 – 0.12	< 0.6 – 2.4	0.52
Cu	0.025 – 0.31	0.13 – 22	< 0.004
Hg	< 0.013	< 0.003	< 0.001
Mo	7,1 - 14	1.1 - 3.0	12
Ni	< 0.13	< 0.2	< 0.2
Pb	17 – 370	220 – 3,400	< 0.0011
Zn	< 1.4 – 580	45 – 340	0.15
NVOC	14 – 46	71 - 780	78

3. THE TREATMENT PROCESS

The process (henceforth referred to as the VKI process) has been developed for treatment of residues from the dry and semidry APC processes (with fly ash admixed with the reaction products) but it may also be applied to the residues from the wet scrubbing process (fly ash and sludge). It is based on an initial aqueous extraction of the residues and a subsequent stabilisation of the washed filter cake with carbon dioxide and/or phosphoric acid. The carbon dioxide source could e.g. be the cleaned flue gas. A diagram of the process is shown in Figure 1.

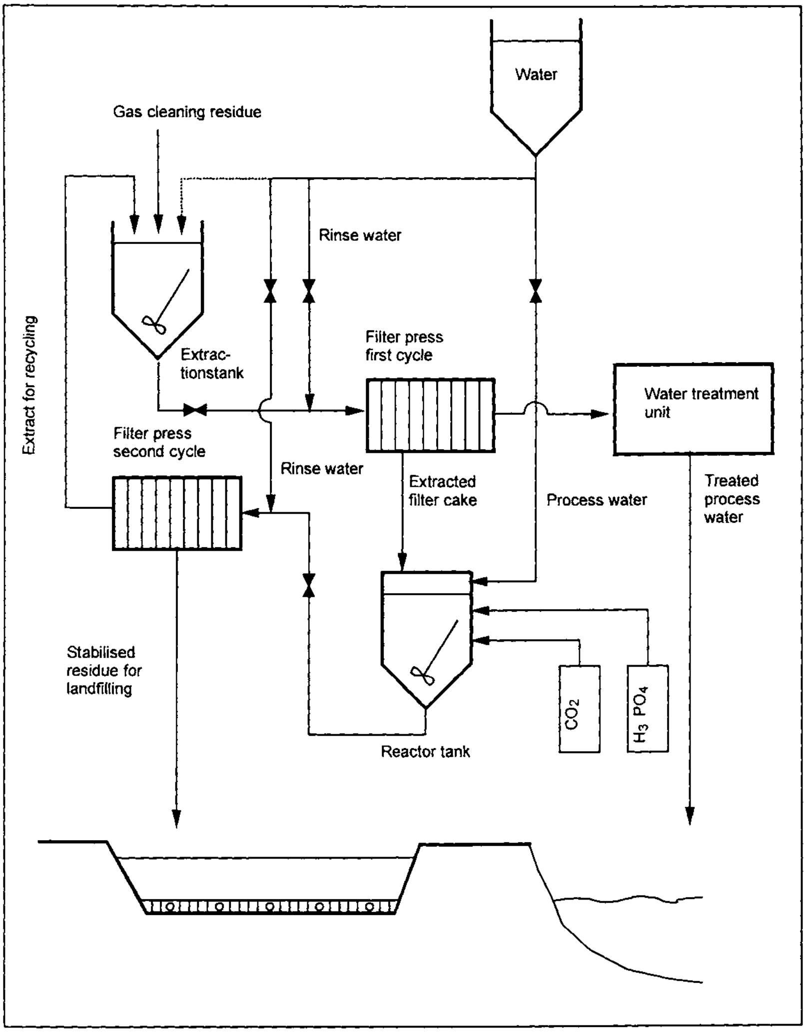

Figure 1
Diagram showing the principle of the VKI treatment process for APC system residues from MSW incinerators.

It was the aim to develop a process which could produce a treated product with a good acidity buffering capacity, a neutral to slightly alkaline pH in contact with water and a low content of soluble salts and trace elements/heavy metals. This was largely achieved during the initial process development period: The original pH of 11.6 of the semidry APC residue was reduced to 10.3 after treatment, and testing of the treated residue exhibited a very substantial reduction of the leachability of salts and most heavy metals/trace elements as compared to the untreated residue. An acid neutralisation capacity of 2.0 eqv/kg (titration to pH = 7.0) was retained. The results indicate that these residues in all probability can be landfilled safely. It has further been shown that the wastewater from the process can be treated by state-of-the-art techniques (pH adjustment and TMT addition followed by flocculation and separation) and subsequently discharged to a municipal wastewater treatment plant or a marine recipient (Hjelmar & Birch, 1997; Hjelmar et al., 1997).

The effectiveness of the treatment may be illustrated by a scenario calculation based on the results of a batch leaching tests performed on untreated and treated APC system residue from a semidry process. The scenario is a landfill of 100 m x 100 m surface area, average depth = 10 m, containing 130000 tonnes (dry weight) of semidry APC residue. The annual rate of infiltration of precipitation is estimated at 250 mm, and the results, which are shown in Table 2, are the total amounts of contaminants released with the leachate from untreated and treated residues, respectively, over a period of 100 years. The scenario is a very simplified one, and ageing effects etc. are not taken into account. The annual amount of leachate produced under these conditions is 2500 m^3.

Table 2
Estimates of the amounts of selected components released with the leachate from a landfill containing 130000 tonnes of semidry APC residues over a period of 100 years. Landfill size: 100 m x 100 m x 10 m.

Parameter	**Untreated residue tonnes**	**Treated residue tonnes**
Chloride	23000	7.8
Sulphate	350	26
Ca	9400	9.9
Na	2400	4.2
K	5100	3.1
As	< 0.02	< 0.0003
Cd	0.005	0.00003
Cr	< 0.003	0.016
Cu	0.94	< 0.0003
Ni	< 0.01	< 0.0003
Pb	200	0.00012
Zn	6.2	0.016

From Table 2 it can be seen that the treatment substantially reduces the expected release of several of the contaminants (most notably chloride, Ca, Na, K, Pb, Cd and Zn) whereas the release of others is reduced less thoroughly (e.g. sulphate) or even increased (Cr). Although the absolute release of Cr (and other oxyanions) is not very large, one of the objectives of the ongoing R&D project is to improve the stabilisation of these components.

In addition to the batch leaching tests referred to above, samples of untreated and washed semidry APC system residue from an MSW incinerator and residue treated by CO_2 alone and by PO_4^{3-} and CO_2 in combination were subjected to pH-static leaching tests at L/S = 5 l/kg. The results, which are presented in Figure 2 for a few components, illustrate the effectiveness of both treatments on the leachability of these components as a function of pH. Although both treatments reduce the leachability of the components substantially, low leachabilities of Pb at low pH values are only achieved using the combined carbon dioxide/phosphoric acid treatment.

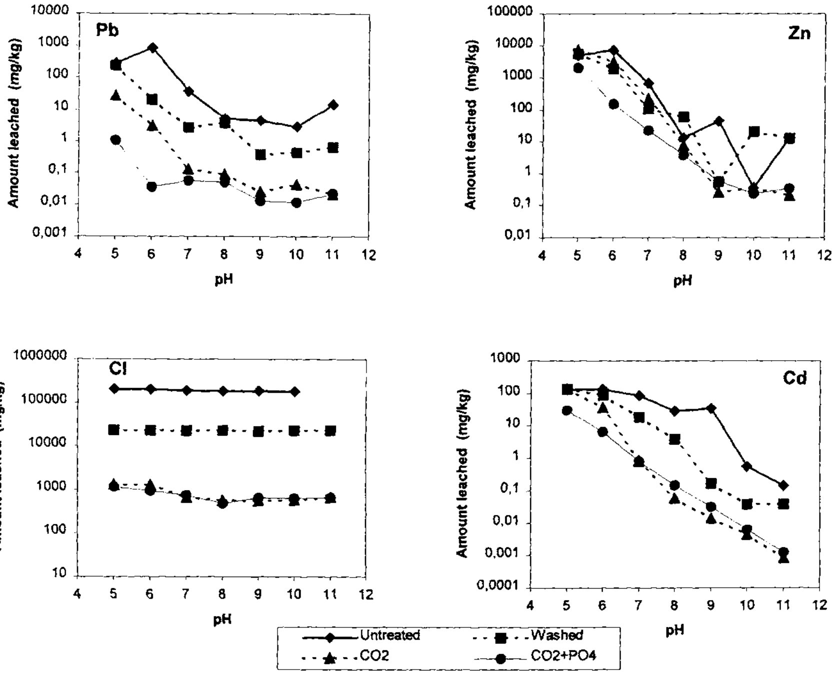

Figure 2
Results of pH-static leaching tests on untreated, washed and treated residues from the semidry APC system at a MSW incinerator. The tests were performed at L/S = 5 l/kg.

4. THE CURRENT R&D PROJECT

4.1 The Pilot Scale Plant

The VKI process is being further developed and optimised in an ongoing R&D project, which was initialised in 1998 and will be completed in 2000. The overall objective of the ongoing project is to prepare the process for full-scale implementation. Activities include further improvement of the stabilised product, minimisation of the consumption of process water through recycling, optimisation of process parameters and reaction conditions, minimisation of the consumption of additives/testing of alternative additives, stabilisation of particularly soluble trace elements and development of an improved understanding of the chemical processes upon which the stabilisation method is based. For this purpose, a large pilot treatment plant has been constructed at the largest MSW incinerator in Denmark, Vestforbraending, see Figure 3.

Figure 3
The pilot scale treatment plant at Vestforbraending.

The tall tank behind the stairways is the reactor tank, and the filter press is visible on the platform in the upper right corner of the picture. The extraction tank is located one floor below this level.

The batch pilot plant which can treat 200 to 800 kg of residue per batch is being used for the experimental work and to demonstrate the effectiveness of the treatment method when applied to residues from the dry/semidry APC processes as well as to fly ash and sludge from the wet scrubbing process.

4.2 Preliminary Results

The initial test runs were used to optimise the sequence of stabiliser addition and minimise the dosages of carbon dioxide alone and carbon dioxide and phosphoric acid in combination as well as to optimise the end-point pH (the reaction control is based on pH measurements) and the retention time in the reaction tank. An end-point pH of 7.0 was chosen. The sequence of addition of stabilising agents did not appear to be critical. Particular efforts were spent trying to minimise phosphoric acid consumption since this is more expensive than carbon dioxide. The carbon dioxide was added as simulated flue gas as a mixture of 10% pure CO_2 and 90% atmospheric air.

The stabilised products from the test runs were subjected to pH-static leaching testing at L/S = 10 l/kg and pH = 5 and 7, respectively. They were also subjected to a 2-stage batch compliance leaching test (a slightly modified version of the draft prEN 12457-3 prepared by CEN/TC 292). Some of the results of the leaching tests on untreated and treated semidry residues are presented in Figure 4 (pH-static tests) and Table 3 (batch compliance tests). Results of pH-static leaching tests performed on untreated and treated fly ash are shown in Figure 5.

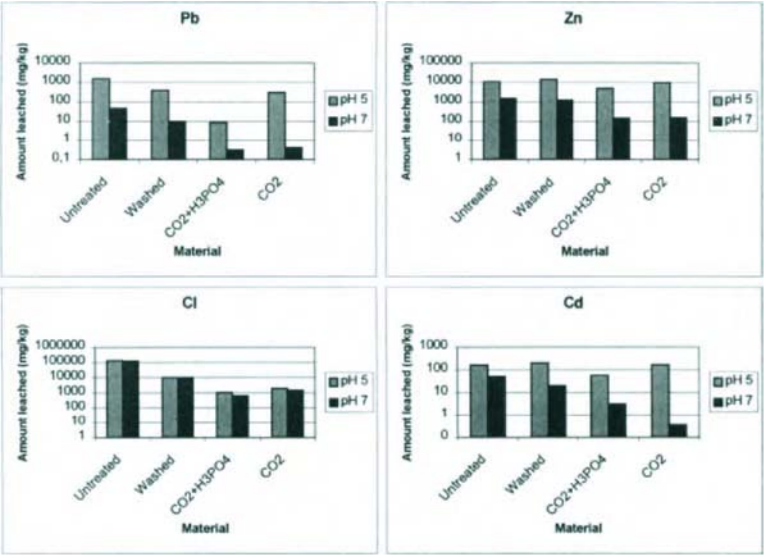

Figure 4 Results of pH-static leaching tests performed at L/S = 10 l/kg on untreated, washed and treated residues from the semidry APC process.

Table 3
Results of 2-stage compliance batch leaching test. The results shown are accumulated leached amounts at L/S = 10 l/kg. The test is slightly modified (using a first step of L/S = 5 l/kg instead of 2 l/kg). The table shows pH values in both eluates.

Parameter	Unit	**CEN draft compliance batch leaching test, prEN 12457-3 (1999)**			
		pH and accumulated leached amounts for L/S = 10 l/kg			
		Untreated residue	**Washed residue**	**Treated residue** $CO_2+H_3PO_4$	**Treated residue** CO_2
pH		11.8/12.5	12.5/12.6	9.6/9.5	9.8/9.8
Chloride	g/kg	140	7.4	0.49	1.2
Sulphate	g/kg	21	15	15	15
As	mg/kg	0.10	< 0.10	0.01	0.01
Cd	mg/kg	0.09	0.04	0.008	0.004
Cr	mg/kg	0.34	0.75	1.8	2.6
Cu	mg/kg	3.5	0.90	0.07	0.04
Hg	mg/kg	0.22	0.08	0.19	0.29
Ni	mg/kg	< 0.05	< 0.04	0.008	0.009
Pb	mg/kg	1800	490	0.07	0.11
Zn	mg/kg	57	29	0.30	0.22

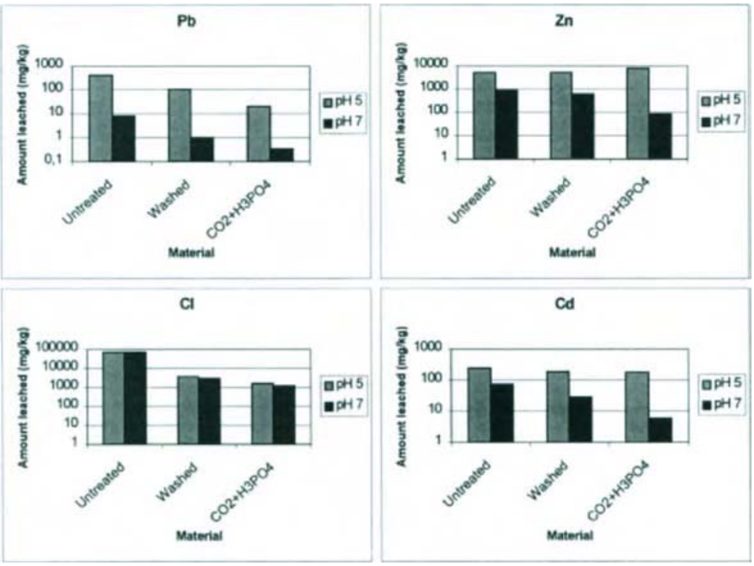

Figure 5 Results of pH-static leaching tests performed on MSWI fly ash at L/S = 10 l/kg.

From Table 3 it can be seen that substantial reductions of the leachability of most contaminants (except for sulphate, Hg and Cr) are achieved with both treatments of semidry APC residue. Further work has been planned to reduce the leachability of sulphate, Hg and Cr (and other oxyanions). Figure 4 confirms the results shown in Figure 2, namely that the addition of phosphoric acid is required to maintain a low leachability of Pb at lower pH values. Table 3 shows that the target values for pH have been achieved successfully. The results in Figure 5 indicate that the fly ash behaves and responds to the treatment in a manner, which is very similar to that of the semidry APC system residues.

4.3 Stabilisation of ACP residues using sewage sludge as a source of phosphoric acid

Laboratory tests have been performed to investigate the possibility of using ash from incineration of sewage sludge as a source of phosphoric acid. Sewage sludge ash is a waste product, which is available in increasing amounts. Due to the exposure to high temperatures, the phosphorus is present in the ash as highly insoluble compounds such as hydroxyapatite ($Ca_5(PO_4)_3OH$) and witlockite ($Ca_3(PO_4)_2$). It is therefore necessary to treat the ash with acid to convert the phosphorus into water-soluble phosphoric acid/phosphates. This could be done using the hydrochloric acid produced by a wet scrubbing system at an incinerator. Thus, laboratory experiments were carried out in which the sewage sludge ash was stirred with 10% of concentrated HCl at L/S 7.5 l/kg for 1 hour before it was used in the stabilisation process as a source of phosphoric acid. This treatment yielded approximately 250 g of PO_4^{3-} / kg of ash on a dry matter basis. Based on experiences with dosing of phosphoric acid from the pilot plant, this means that 50 to 150 kg of sewage sludge ash will be required to stabilise 1 tonne of semidry APC residue. Results of pH-static leaching tests on a semidry APC residue stabilised with sewage sludge and other stabilised products ash are shown in Figure 6.

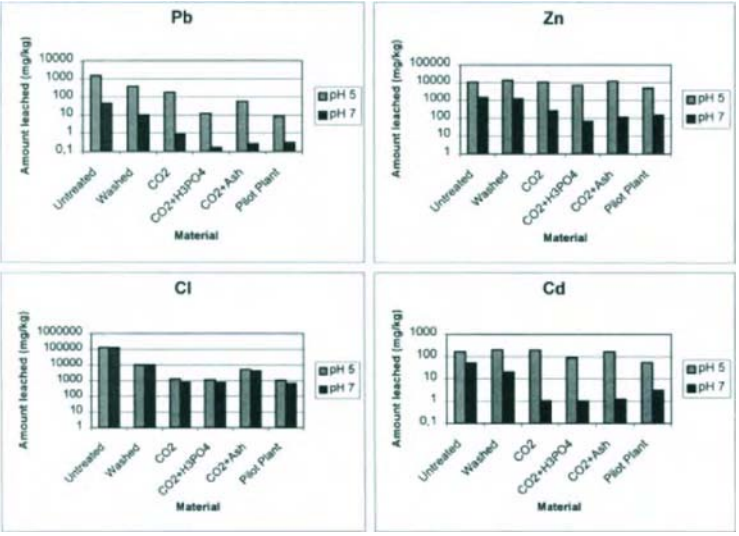

Figure 6
Results of pH-static leaching tests at L/S = 10 l/kg on semidry APC residue stabilised in the lab with CO_2, CO_2+phosphoric acid (also in pilot scale) and CO_2 + sewage sludge ash.

From Figure 6 it can be seen that for the residues leached at pH = 7, all the stabilisation methods tested reduced the leaching of the heavy metals from the residues significantly. At this pH, the quality of the residue treated with CO_2 and sewage sludge ash was comparable to the quality of the residue treated with CO_2 and commercially available phosphoric acid. Leaching at more extreme conditions (pH = 5) showed that the treatment procedures were effective only for Pb under these conditions, and that stabilising using phosphoric acid (including the sewage sludge ash) gave the best results for Pb.

5. CONCLUSIONS

It has previously been demonstrated that a process for treatment of semidry and dry APC system residues from MSW incinerators based on an initial aqueous extraction followed by re-suspension and stabilisation of the filter cake with phosphoric acid and/or carbon dioxide can produce a material with vastly improved disposal properties. A 2.5 year R&D project was initiated in 1998 with the objective to optimise and prepare the process for full-scale implementation, and to extend the applicability of the process to include fly ash and wet scrubber sludge. Most of the process optimisation and adjustment work is being carried out on a large-scale batch pilot treatment plant, which has been constructed at a large MSW incinerator in Copenhagen. The quality of the stabilised residues are evaluated on the basis of the results of pH-static leaching tests and batch leaching tests. Preliminary results indicate that good stabilisation results can be achieved for most components using carbon dioxide and phosphoric acid, both for semidry residues and fly ash. Using CO_2 alone also yields good results, but with higher leachability of Pb at low pH values. Further work is being carried out to reduce the leaching of sulphate and Hg as well as Cr and other oxyanions. Test results indicate that it may be feasible to use sewage sludge ash as a source of phosphoric acid.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Recycled Aggregate Concrete Sound Barriers for Urban Freeways

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An increased rate of construction and demolition (C&D) waste generation in the Melbourne metropolitan area has a two-way impact, viz., a rapidly disappearing available landfill space and depletion of natural resources. As a result, there is government and community pressure to reduce the volume of waste by recycling of the waste material and the reuse of its products. This paper focuses on the enhancement of concrete waste products to improve their use in the manufacture of new products. This approach has already resulted in the confirmation that Recycled Concrete Aggregate (RCAG) can be a suitable substitution for the coarse aggregate fraction in production of pre-mixed concrete. The current research focus is on understanding of two of the properties of RCAG and their impacts on strength, durability and the acoustic performance of new concrete. Firstly, the presence of any chemical impurities and their effect on microstructure development, and secondly, the porosity of the cement paste component of the aggregate and its effect on the acoustic performance of concrete, made from RCAG, are examined. The aim of the research is to develop structurally sound Recycled Aggregate Concrete (RAC) with a good sound absorbing characteristics, and to use it in the manufacture of sound barriers for urban freeways. Preliminary results clearly indicate that the porosity of RCAG is more than that of normal concrete aggregate and this has an advantageous impact on the sound absorption coefficient of RAC, and that the strength of such concrete is more than adequate for the intended application.

KEYWORDS

Concrete recycling, aggregate, chemical contamination, porosity, sound absorbing concrete, sound barriers.

1. INTRODUCTION

The amount of unwanted, partially used, rejected or unused materials from C&D sites in Victoria, Australia, is continually growing as a result of the current construction boom responding to the demand for new infrastructure and housing. There are two usual ways of dealing with waste materials, firstly, the most common, treating them as a waste and secondly, recognising the value of some of them for recycling and reuse. The amount of C&D waste deposited at licensed landfill sites in metropolitan Melbourne, according to the latest survey (Nolan, 1998) accounts for up to 70% of total waste going to landfill sites. The main component of C&D waste is concrete rubble, which accounts for 25% by weight. There is also a significant amount of concrete waste used as fill. In total, approximately 700,000 tonnes of concrete rubble is not reused and, at the same time, occupies limited landfill space unnecessarily.

Fortunately, the construction and demolition industry has realised that most of C&D waste can be separated at source, then recycled and reused in infrastructure projects. Recycling and reuse of reprocessed waste is now seen by the industry as economically sound and feasible. Concrete waste minimisation, concrete recycling and reuse of its products can save scarce landfill space and reduce exploitation of natural resources, such as crushed rock. The proliferation of recycling plants also reduces resources related to transport of the demolition products. Besides the industry initiatives, the Victorian Government has created a supportive environment for concrete recycling and the reuse of its products. An example is VicRoads' specification for crushed concrete in road sub-base layers, and the recently written guidelines for crushed concrete aggregate for concrete production, (CSIRO, 1998). Another example is the provision of research funds through EcoRecycle. Such approach to C&D waste, and the synergy between private industry and the government agencies has resulted in 750,000 tonnes of RCA being reused in new infrastructure projects last financial year (1998/9).

2. THE NEED FOR NEW APPLICATIONS FOR RECYCLED CONCRETE PRODUCTS

A range of recycled concrete products is manufactured by a small number of private companies and some municipalities, mainly in the metropolitan Melbourne area. These products include various maximum/nominal sizes of Class 4, 3, and 2 crushed concrete and cement treated crushed concrete. The manufacturers have the necessary expertise and plant in place to produce quality RCAG of any desirable grading, with a very low level of foreign materials present. The products conform to Australian, VicRoads (State Road Authority) and industry specifications, and are well accepted by the construction industry in present applications. These include fill material, substitute for crushed rock in sub-base or base layers in roads construction, and as a bedding material in drainage construction

One of the means of reducing the landfill volume and preserving of finite natural resources is by the reuse of the material in an innovative manner. At present in Victoria, RCAG is mainly used as a substitute for virgin quarry material in road construction. Although, in these applications, the life of original concrete is extended, the value and potential of this material is buried irrevocably in the ground under the final layer of asphalt. To extend the useful life of this resource further, and to utilise fully its potential more sophisticated applications of RCA are needed.

Recently, EcoRecycle Victoria commissioned a research project undertaken by CSIRO aimed at increasing the use of locally available RCAG in pre-mixed concrete by producing a new product, Recycled Aggregate Concrete (RAC). The trial projects resulted in the substitution in the concrete mix, of natural crushed rock ranging from 20 to 100% of coarse fraction, with RCAG. The RAC was used in footpath construction. Introduction of RAC was possible because of the perseverance of experts from Alex Fraser Limited in Victoria and their perception that RCAG was under utilised in road works. Researchers from CSIRO have supported this view and concluded that RCAG can be used in non-structural concrete, (CSIRO, 1998). However, there is still some reluctance within the construction industry to use concrete incorporating recycled aggregate and only full technical data, tests and performance reports can provide necessary evidence.

In the light of the demand for widening the range of application for RCAG, the aim of this research is to develop concrete that will incorporate RCAG for use in sound absorbing concrete barriers. The reprocessed concrete waste is investigated to determine the presence of any chemical impurities and whether these impurities have potential detrimental effect on the hydration of cement and therefore development of concrete microstructure. The other property of RCA under examination is the porosity of the cement paste component of the aggregate and its effect on the acoustic performance of new concrete.

3. EXPERIMENTAL PROGRAM

The experimental activities of the research are divided into three main phases:

1. RCAG examination (material characterisation).
2. RAC (material) development.
3. Sound barriers (product) development.

In the first phase, the basic engineering properties of the aggregate are confirmed for the purpose of the concrete mix design and then the cement paste is separated from the natural stone component and examined for the presence of any chemical impurities and porosity. The undisturbed cement paste is examined for the interconnected permeable voids using the conventional Apparent Volume of Permeable Voids (AVPV) test and micro-porosity using nitrogen adsorption and neutron scattering techniques. Further, samples of 600μ powdered cement paste are used to determine the chemical composition using Scanning Electron Microscopy (SEM), X-ray diffraction and neutron scattering techniques. The data obtained is used in the development of Sound Absorbing Recycled Aggregate Concrete (SA-RAC) which is plain concrete to be used for the development of sound barriers for urban freeways.

4. RCAG EXAMINATION

14/10mm Class 2 Crushed Concrete supplied by Alex Fraser Limited is being examined as the material of the highest quality that has the mechanical characteristics that make it an ideal substitution for coarse aggregate fraction in new concrete. The aggregate is a product of the additional screening of 20mm Class 2 Crushed Concrete, eliminating particles smaller than 13.6mm. Batches of the aggregate are being taken, on monthly basis, from stockpiles at the company's Laverton North recycling plant for examination of the RCAG and production of RAC. The aggregate is practically free from any visible contamination and has a rounded shape. Although the basic engineering properties such as crushing value, maximum dry density (MDD), particle size distribution, water absorption of any RCA supplied by the aggregate manufacturer are well defined, some of them are being confirmed for the accurate mix design. The fine fraction, which is the by-product of concrete recycling, is also being investigated for any chemical contamination and its suitability for incorporation in a new concrete production. In this research, however, the main focus is on the determination of the percentage of cement paste residue in RCA, its chemical composition and porosity of cement paste residue.

5. CEMENT PASTE RESIDUE IN RCAG

RCAG is the product of demolished concrete when subjected to crushing and sieving processes. It consists of cement paste of original concrete adhering to natural stone. The concrete rubble used for the production of RCA is of miscellaneous origins, varying compressive strengths, age and exposure conditions. These factors, as well as the quantity of cement paste component in RCA, affect the basic engineering properties of the aggregate and ultimately properties of RAC.

The cement paste component lowers the MDD of RCAG, which in turn influences the density and acoustic properties of any concrete made from RCAG. To determine the percentage of cement paste residue in RCAG, the aggregate was broken down using a laboratory jaw crusher and the natural stone was separated by hand. The average amounts of cement paste are shown in Table 1.

Table 1
Percentage of cement paste in RCA

Batch – (Date)	Samples	Average % of cement paste residue
RCA-1 - (10/06/99)	1.1, .2, .3, .4, .5	19
RCA-2 - (05/07/99)	2.1, .2, .3, .4, .5	19
RCA-3 - (18/08/99)	3.1, .2, .3, .4, .5	16

Despite the lower density, the cement paste component is presumed to have much higher porosity than basalt, which is the natural aggregate extensively, used in the production of concrete in Melbourne. This porosity, and the lower density, contributes to increased sound attenuation capacity of RAC. However, increased porosity results in more permeable material and original concrete could be infiltrated by chemical contaminants during its service life.

6. CHEMICAL IMPURITIES IN RCAG

Concrete gains its strength by a process known as hydration of cement that results in hardened cement paste coating fine and coarse aggregate. The full cement hydration, and therefore desirable microstructure development, is only possible if there is an exact amount of water for chemical reactions to take place and if these reactions are not adversely affected by compounds other then those characteristic of cementitious materials.

A Scanning Electron Microscope (SEM) was used to examine composition of elements in RCAG cement paste. Representative samples were obtained from separated cement paste residue of each batch of RCAG and ground to a 600μ powder. The results show that, in the samples examined, there were no significant amounts of chemical contaminants in comparison to the control sample (pure cement paste). However, there is a slight increase in the sulphur, chlorine and iron content in RCAG, which is attributed to possible exposure of the aggregate to sulphur dioxide in the air and to surface and ground water. Figure 1 presents the relative elementary composition of cement paste of the samples under examination.

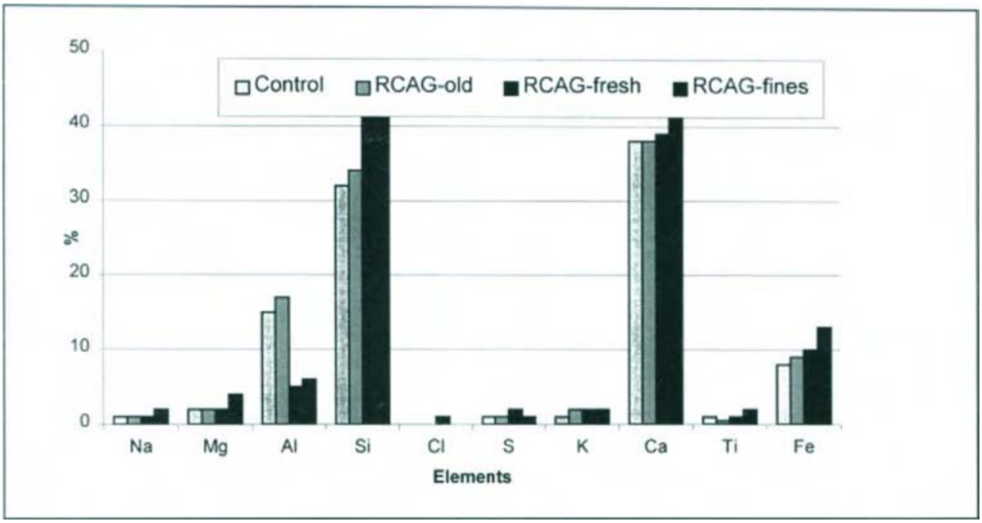

Figure 1. Elements in cement paste

In order to verify and complement SEM data, the same source and sample preparation procedures were used for examination using an X-ray diffraction and Medium Resolution Powder Diffractometer (MRPD) at the Nuclear Science and Technology Centre at Lucas Heights in Sydney. MRPD is a relatively new neutron scattering technique capable of characterising real time phase development and chemistry of concrete (Livingston, 1995). The preliminary interpretation of data obtained using X-ray diffraction and MRPD indicates that there is no significant difference between control (fresh concrete paste) and recycled pastes in terms of compounds present.

7. POROSITY OF RCAG

Porosity of the cement paste of RCAG is due mainly to gel and capillary pores forming during the hydration process in the original concrete. This can be the result of the formation of entrapped or purposely introduced air voids, as well as an effect of the weathering processes during the service life of concrete. The porosity of RCAG affects density, permeability and durability of RAC, and consequently sound absorption capacity and sound transmission loss in new concrete. A number of tests have been adopted to determine porosity of the cement paste component, ranging from conventional AVPV test, through nitrogen absorption using Micromeretics Gas Adsorption Surface Area (MGASA) analyser to Small Angle Neutron Scattering (SANS) using neutron scattering technology. Firstly, samples of cement paste pieces where examined using SANS as it is a non-destructive test method, (Livingston, 1995). The same samples were further used for porosity examination using MGASA analyser and finally subjected to AVPV test.

To show the porous nature of cement paste and to indicate the difference in micro-porosity between RCAG and normally used natural coarse aggregate for concrete production, basalt aggregate was examined using MGASA analyser. The results of these tests are presented in Table 2 and clearly indicate that overall RCAG is 60% more porous than natural crushed rock. The micro porosity of the last batch examined confirms results from previously tested cement pastes.

Table 2
Porosity, pore size and surface area of the aggregate

Sample	Apparent Volume of Permeable Voids	MGASA- Ave. pore size	MGASA-pore volume
	[%]	[Angstrom]	[cm^3/g]
Basalt-1	-	92.6	0.0073
RCA-2.2 (05/07/99)	20	156.6	0.039
RCA-3.2 (18/08/99)	19	149.8	0.041

8. SA-RAC DEVELOPMENT

The objective behind the development of this concrete is to incorporate 100% of coarse recycled aggregate and up to 30% of cementitious supplement, mainly fly ash, and make the concrete robust and sound absorbing. The target strength for RAC is 15MPa, which is an adequate strength to withstand loads imposed on a concrete sound barrier. The mix design of RAC is based on basic engineering properties and porosity data of the aggregate obtained in the previous stage of the research. Table 3 presents density and water absorption of RCAG.

Table 3
Maximum Dry Density and Moisture Content of RCA

Batch – (date)	Samples	Average MDD	Average Water Absorption
		[kg/m^3]	[%]
RCA-1 - (10/06/99)	1.1, .2, .3, .4, .5	2270	6.0
RCA-2 - (05/07/99)	2.1, .2, .3 .4, .5	2290	6.6
RCA-3 - (18/08/99)	3.1, .2, .3, .4,.5	2220	6.4

Because the rate of strength gain in RAC will not be a crucial factor, some of the mix designs under investigation incorporate up to 30% of fly ash substitution for ordinary Portland cement. The effect of fly ash substitution on compressive strength at 28 days is minimal, and on average decreases it by 10%. Due to the lower density of RCAG, the density of new concrete is on average 10% lower than that of normal density concrete. The lower density and consequently higher porosity of RCAG, and thus the RAC, increases the sound absorption characteristics of the new concrete. Table 4 shows density and compressive strength test results of RAC.

Table 4
Density and compressive strength of RAC

Sample – Batch (date)	Density [kg/m³] @ 28 days	Average compressive strength [MPa]	
		7days	28days
RAC-1 - (10/06/99)	2069	9.3	15.6
RAC-2 - (05/07/99)	2096	9.5	15.0
RAC-3 - (18/08/99)	1945	9.9	14.7

Cement paste of fresh RAC separated from natural stone, and undisturbed pieces, and/or 600μ powder are examined using AVPV test, SEM, X-ray diffraction, MGASA, MRPD and SANS. The most important test is the examination of the microstructure development in new concrete using MRPD.

Using a modified mix design, the inherent sound absorbing characteristics are further enhanced by the employment of a grading deficiency concept, which results in the introduction of interconnected air voids into new concrete. The porosity is further altered in some mix designs by air entraining additives. Concrete specimens (82mm in diameter, 100mm long) were prepared to determine acoustic performance of this new concrete (SA-RAC). The density, total volume of voids, AVPV and micro-porosity of four samples of SA-RAC are presented in Table 5.

Table 5
Density and porosity of SA-RAC

Sample	Density [kg/m³]	Total voids volume [%]	AVPV [%]	Volume of micro-porosity [cm³/g]
SUT-1	1770	20.1	15	0.051
SUT-2	1819	16.7	16	0.034
SUT-3	1767	22.3	16	0.027
SUT-4(100)	2096	12.0	14	Not available

Sound absorption of any material can be expressed by two indices, viz., the sound absorption coefficient (alpha) and the noise reduction coefficient (NRC). An impedance tube was used to obtain the sound absorption coefficient (alpha) in the frequency band characteristic to those of traffic noise (63 to 2000Hz), where the loudest traffic noise from heavy vehicles is between the frequencies of 100 Hz and 1000 Hz, (Beranek, 1992). Table 6 shows the statistical sound absorption coefficient, NRC and water absorption of the investigated samples. It is noted that NRC and alpha for normal density plain concrete were found to be virtually zero.

Table 6
Acoustic characteristics of SA-RAC

Sample	Water Absorption	Sound Absorption Coefft.	Noise Reduction Coefft.
	[%]	Alpha	NRC
SUT-1	4.3	0.25	0.31
SUT-2	4.0	0.31	0.49
SUT-3	3.6	0.26	0.28
SUT-4(100)	7.1	0.20	0.22

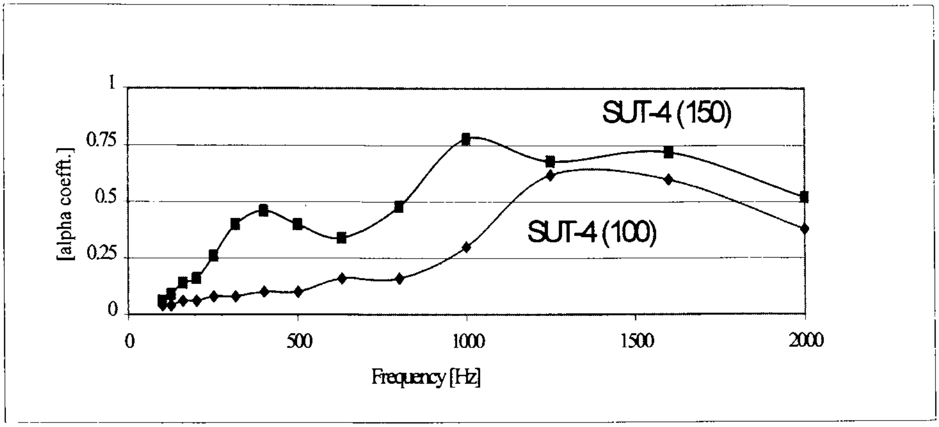

Figure 3. Affect of thickness of RAC on sound absorption coefficient

The acoustic performance of SUT-4 (150) was compared with two sound barrier systems, viz., the "Soundtrap" system, purposely designed to absorb traffic noise, and the "Noisebloc" system designed as a sound reflective barrier. The comparison of performance is shown in Figure 4.

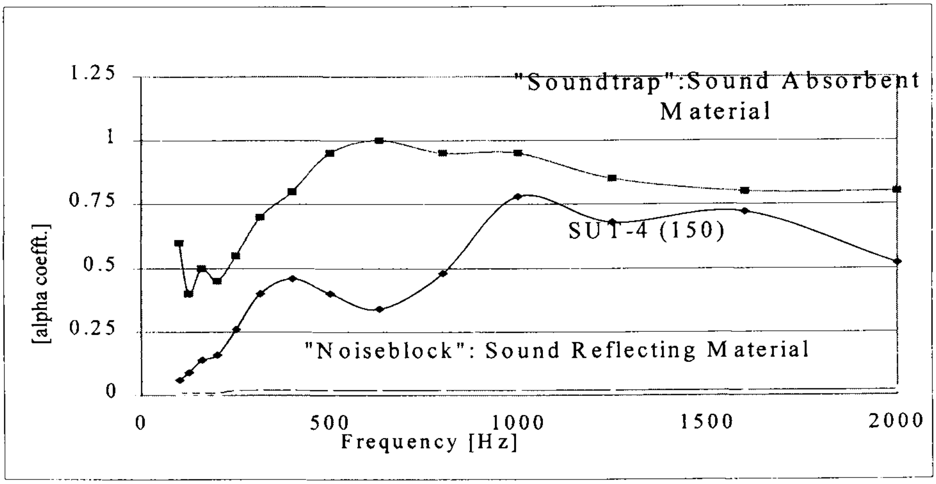

Figure 4. Comparison of acoustic properties of sound barrier systems

In a further development, the thickness of the sample SUT-4 was increased to 150mm, as this is the optimal thickness of most sound absorption barriers. This enabled a comparison between the performance of different barrier systems. Figure 3 shows the difference between sound absorption coefficients alpha of SUT-4 (100) and SUT-4 (150).

9. DISCUSSION

The preliminary findings indicate that RCAG has engineering properties that make it a suitable substitution for coarse aggregate in the production of concrete in regard to strength. These findings support already existing evidence that crushed concrete waste, if properly reprocessed, constitutes a valuable construction material, (CSIRO, 1998). No significant level of chemical impurities is present in samples of RCAG examined and therefore there is no abnormal microstructure development in RAC. It is also evident that inherent porosity, if utilised and enhanced in a certain manner, can lead to the development of porous concrete that absorbs sound energy. The sound absorption coefficient is on average 3.7 times higher than that of the control normal density concrete, this indicates that there is the link between porosity of RCAG and RAC and the enhancement of its sound absorbent characteristics.

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G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Substance Flow Analysis of Persistent Toxic Substances in the Recycling Process of Municipal Solid Waste Incineration Residues

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This study analyzes the substance flow such as heavy metals and dioxins in the process of recycling these residues containing slugs, and studies possible recycling of various residues, while making comparison with the standards for heavy metals and PCDDs/DFs regarding soil and water quality.

1. INTRODUCTION

Approximately 50,000,000 tons of municipal solid wastes are discharged in Japan every year, and 70% of them are incinerated from the viewpoint of sanitation and reducing waste volume [1). The incineration residue generated in this process reaches an annual level of 6,000,000 tons, and almost all of them are subjected to landfill disposal. It is important to reduce the volume of municipal solid waste and to promote material recycling. In addition to these efforts, use of the melting slag formed from municipal solid waste and incineration residue with the melting furnace, and balanced recycling of incineration bottom ash are important techniques for adequate treatment and recovery of resources. This concept agrees with that of WASCON which encourages simultaneous promotion of recycling of the municipal solid waste to use it as construction material, and environmental protection [2). These incineration residues contain heavy metals and dioxins (PCDDs/DFs) as persistent toxic substances. So management of these incineration residues require both preservation of resources by recycling and prevention of environmental pollution resulting from hazardous substances. In Japan, the leaching value of heavy metals for the slag molten in high temperature is set up in the regulatory standards for heavy metals related to the recycling of incineration residue [3). For other residues, standards are stipulated for them when finally disposed at the managed disposal site. For PCDDs/DFs, on the other hand, there is a target of reducing the 1997 level of the total emissions by 90% [4). This study analyzes the substance flow such as heavy metals and dioxins in the process of recycling these residues containing slugs, and studies possible recycling of various residues, while making comparison with the standards for heavy metals and PCDDs/DFs regarding soil and water quality. In particular, study has been made on the contents of hazardous substances and leaching behavior in the incineration residue and in the process of melting the incineration residue. In this paper, incineration fly ash and incineration bottom ash are collectively described as incineration residues, and incineration bottom ash and incineration fly ash may be abbreviated as bottom ash and fly ash.

2. CONTENT OF HAZARDOUS SUBSTANCES IN INCINERATION RESIDUE

We have summarized the content of hazardous substances contained in the municipal solid waste incineration fly ash, incineration bottom ash, melting slag and fly ash generated during melting (hereinafter referred to as "melting fly ash") [5-43). The substances to be studied are as follows; Pb as a hazardous substance contained densely in incineration residue was examined as a heavy metal, and PCDDs/DFs was studied as a persistent toxic substance. Fig. 1 shows the distribution of Pb content (mg/kg-dry) in fly ash, bottom ash, melting slag and

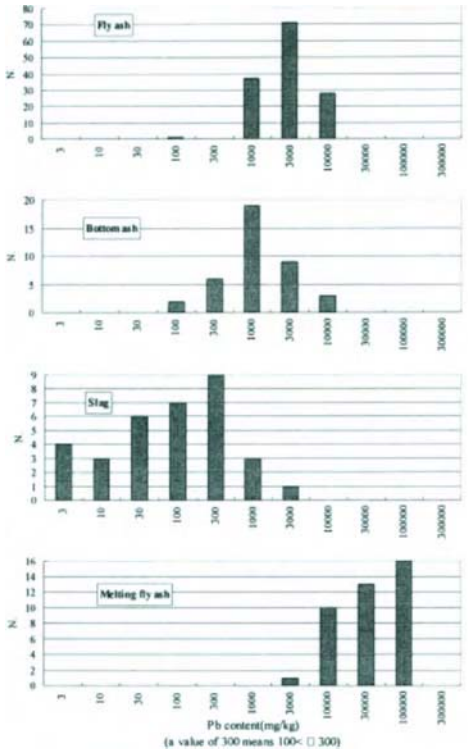

Fig.1 The distribution of Pb content in incineration residue

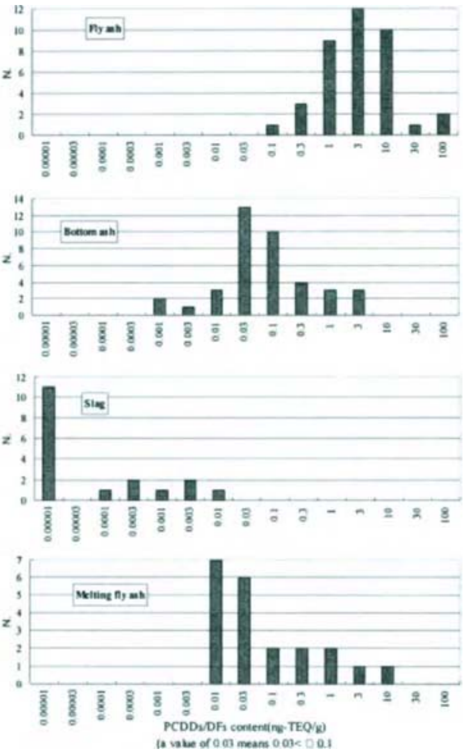

Fig. 2 The distribution of PCDDs/DFs content in incineration residue

melting fly ash, and Table 1 illustrates the statistic value (number of samples, maximum value, minimum value, average value, median value and mode value). Pb is evaporated once in the high-temperature waste incineration and residues melting process. After that, Pb is densely concentrated in fly ash and melting fly ash, while Pb content is smaller in slag and bottom ash which is the residue of evaporated heavy metals. The result of examining the Pb content in the soil of the Japanese urban district shows that Pb content regarded as contaminating the environment is 600mg/kg [44). When this is compared with the median values of slag and bottom ash respectively given as 92mg/kg and 555mg/kg, the greater portion of slag and about half of bottom ash show the levels below this value.

Table 1 The statistic value of incineration residues

Component	Statistic value	Fly ash	Bottom ash	Slag	Melting fly ash
Pb	N.	137	39	33	40
(mg/kg)	AVE.	2146	886	145	28351
	MAX.	8290	3700	1240	100000
	MIN.	91.9	85.0	0.005	2200
	MED.	1650	555	92	19000
	MOD.	1290	1000	100	19000
PCDDs+PCDFs	N.	38	39	18	21
(ng-TEQ/g)	AVE.	6.54	0.20	0.001	0.33
	MAX.	100	1.50	0.010	3.50
	MIN.	0.069	0.00070	0.00000	0.0041
	MED.	2.0	0.032	0.00000	0.016
	MOD.	1.7	0.016	0.00000	0.25

Fig. 2 shows the distribution of PCDDs/DFs content (ng-TEQ/g-dry), while Table 1 represents its statistic value. Fly ash contain the highest percentage of the PCDDs/DFs content. Incineration bottom ash and melting fly ash contain about the same percentage. Slag exhibits the lowest figure. The average values of slag and bottom ash are 0.001 ng-TEQ/g and 0.20 ng-TEQ/g, respectively. The median values are 0.00000ng-TEQ/g and 0.032ng-TEQ/g respectively. Slag exhibits an overwhelmingly low value. The concentration of PCDDs/DFs which requires some effective measures to be taken for soil is said to be 1 ng-TEQ/g [45). Most of the fly ash are shows the level above this concentration. On the other hand, the greater portion of bottom ash and melting fly ash show the value below 1 ng-TEQ/g. The melting slag provides the background level of soil. Fly ash exhibit a great percentage of heavy metal content as well as PCDDs/DFs content. This has again demonstrated the need for its proper management.

3. LEACHING OF HAZARDOUS SUBSTANCES FROM INCINERATION RESIDUES

3.1. Pb leaching behavior

Fig. 3 shows the leaching concentration of Pb in various batch type leaching tests of slag, fly ash, combined ash and bottom ash, where it represented as leaching behavior for pH [46).

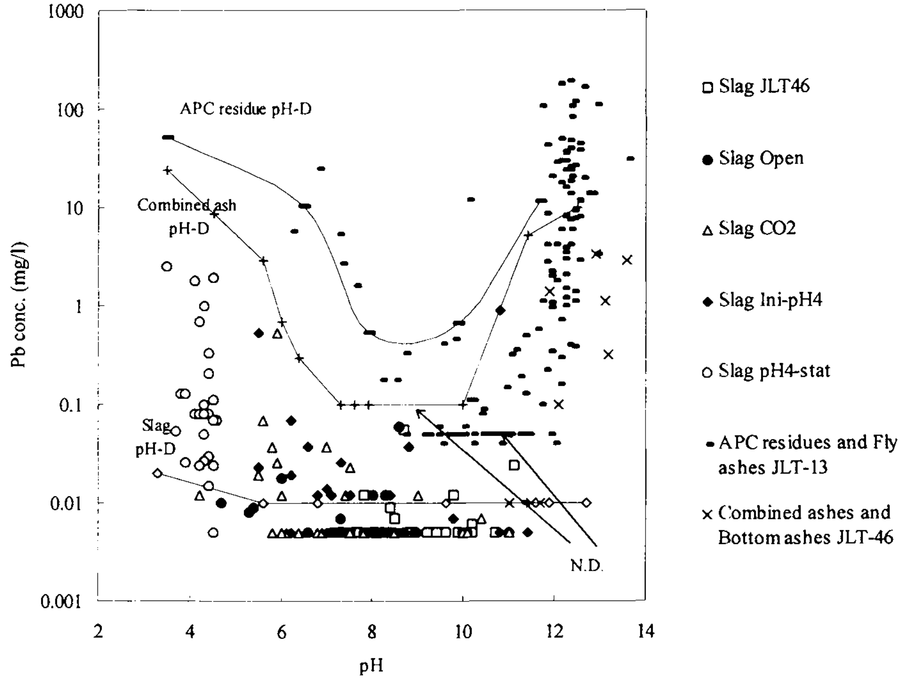

Fig. 3 Leaching behavior of Pb from residues in various batch leaching tests

Here JLT46 denotes an leaching test method for the Japanese soil where the test is conducted by filtering with the membrane filter with a hole diameter of 0.45μm after shaking of the test sample for 6 hours, using a sample particle size of 2mm or less, distilled water and L/SIO. JLT13 is the same as JLT46 except that the sample particle size is 5mm or less and the glass filter having a hole diameter of 1μm is used for filtering. The pH-dependent test is a test where HNO3 or NaOH are used as the final pH of L/SIO and leachate is different and the sample is shaken for 6 hours. In this test, solution of nitric acid and solution saturated with carbon dioxide gas are used as solvents for Ini-pH4 and CO2, respectively, and the samples are shaken for 6 hours after the initial pH is adjusted to 4. Furthermore, the Open or pH4-stat test is an leaching test where the sample is shaken by the stirrer for 6 hours. Leachate is open to air in both Open and pH-stat test methods.

In the pH4-stat test method, pH controller and nitric acid are used to ensure that pH value of the leachate is maintained at 4. Independently of the type of leaching, both slag and incineration residue shows a pH-dependent leaching behavior characteristic of Pb as amphoteric metal. This shows that the leaching concentration of Pb is high in the low-pH and high-pH areas, and the pH value is one of the most important Pb leaching factors. Therefore, for adequate management of the residue, it is important to keep track of such leaching behavior in addition to the determined leaching test method placed under regulation [47, 48). When compared with the incineration residue, the slag has the leaching concentration of Pb much smaller at any pH level. With respect to leaching from slag, pH is slightly lower in the Ini-pH4 method and CO2 method than that of the leaching test (JLT46) using pure water. Pb leaching concentration tends to be slightly higher. Despite that, leaching concentration is extremely low. Furthermore, the leaching concentration of Pb is almost the same between the following two cases; the case where pH for slag is acid and the case where pH for bottom ash is slightly alkaline. This shows that leaching of the heavy metal depends on pH. On the other hand, it is important to keep track of what pH level the residue assumes in the environment, depending on actual environmental conditions and properties of the residues such as acid neutralization capacity. This is an important factor having a serious impact on leaching of the heavy metal.It is reported that, when the content of carbonate in clay is high, pH buffer capacity is high and Pb adsorption capacity is high [49).

Table 2 Outline of leaching test method

Test name	**JLT-46**	**Open**	**CO_2**	**Ini-pH4**	**pH4-stat**	**Availability test (NEN734)**
Leaching vessel	1 L polyethylene bottle	1 L glass beaker	1 L polyethylene bottle	1 L polyethylene bottle	1 L glass beaker	1 L glass beaker
Sample preparation	< 2 mm, 10-30 mm	< 2 mm, 10-30 mm	< 2 mm, 10-30 mm	< 2 mm, 10-30 mm	< 2 mm, 10-30 mm	< 125 μm
Sample mass	50 g	50 g	50 g	50 g	50 g	16 g
Leachant	Distilled water	Distilled water	Water saturated with CO_2 (pH4)	Water adjusted to pH4 with HNO_3	Distilled water acidified by HNO_3, pH controlled at 4	Distilled water acidified by HNO3, pH controlled at 7 and 4
Liquid to solid ratio	10	10	10	10	10	50 × 2
Number of leachant	1	1	1	1	1	2
Agitation	Horizontal translation (200 times per min, 40-50 mm width)	Magnetic stirrer (10-30 mm sample placed on polyethylene net)	Horizontal translation (200 times per min, 40-50 mm width)	Horizontal translation (200 times per min, 40-50 mm width)	Magnetic stirrer (10-30 mm sample placed on polyethylene net)	Magnetic stirrer
Leaching time	6 h	6 h	6 h	6 h	6 h	3 h × 2
Leachate separation	0.45 μm filtration	0.45 μm filtration	0.45 μm filtration	0.45 μm filtration	0.45 μm filtration	0.45 μm filtration

It is also reported that neutral leachate is obtained at the disposal site because of reduction in the pH value of leachate itself, not because of reduction in the pH of the residue itself [50). Buffer capacity can be expected from aged bottom ash and other residue where carbonate content is high. Regarding leaching of heavy metals, it is also important to study transition of pH values in the environment from the viewpoint of this acid neutralization capacity and its factors.

3.2. Leaching behavior of PCDDs/DFs

Fig. 4 shows the distribution of leaching concentration of fly ash with high PCDDs/DFs content and fly ash treated by cement and heavy metal stabilizer. It contains the data of leachate based on the JLT13 (L/S1O and distilled water used) [42). It does not show a comparison of the same samples. However, when comparison is made between the mode value of 1.7 ng-TEQ/g for the PCDDs/DFs content of the above-mentioned fly ash, and the mode value of 0.11 pg-TEQ/L for this leaching concentration, PCDDs/DFs content in a small amount of 10^{-5} to 10^{-4} % is leached from fly ash. PCDDs/DFs leaching from the fly ash was studied by Carsch et. al. [51). In the 8-day batch leaching test using 100g of fly ash per liter of distilled water, 20 ng/L of HpCDD and 40 ng/L of OCDD were detected. In the 2 week leaching test using 1 kg of fly ash for ten liters of distilled water, 20 ng/L of HpCDD and 30 ng/L of OCDD were detected. On the other hand, Berbenni et. al. considers that the leachate of fly ash from the EP is less than 20ng/L in terms of the concentration of each homologue [52). The detection range of fly ash leaching concentration this time is 0.03 to 30pg-TEQ/L, which corresponds to about 0.003 to 3 ng/L in terms of total concentration.

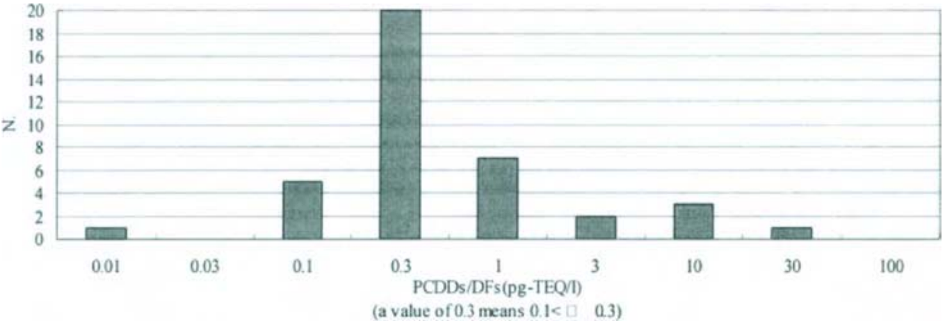

Fig. 4 Distribution of leaching concentration of fly ash

So this is not detected according to the example of Berbenni et. al. Incidentally, solubility of dioxins obtained by Friesen et. al. is 4.4 ng/L for 1,2,3,4,7,8-HxCDD, 2.4ng/L for 1,2,3,4,6,7,8-HpCDD, and 0.4 ng/L for for OCDD [53). Leaching concentration detected this time is a sufficiently attainable level, when viewed from solubility. However, leaching rate of the PCDDs/DFs from fly ash is low. This will be because of strong power of adsorption to ash. Also, the median value of leaching value of PCDDs/DFs from fly ash is 0.22 pg-TEQ/L. When compared with the proposed environmental standard value for water quality amounting to 1.0 pg-TEQ/L [54), 80% or more meets this standard. Only one type of the sample exceed the proposed standard value of 10pg-TEQ/L for waste water. However, Oil content, solvent, surfactant, humic substance and the like are considered to facilitate leaching of PCDDs/DFs [55 - 56). Survey of these factors and leaching behavior from bottom ash and melting fly ash containing little carbon content is not sufficient. It is important to examine ash types and leaching acceleration factors, and to investigate the leaching test method including the size of the filter paper for the study of impact of fine particulates. It is also essential to make evaluation on the level of a trace quantity with consideration given to concentration of PCDDs/DFs in the living system from the water environment system.

4. FLOW OF HAZARDOUS SUBSTANCES IN INCINERATION RESIDUE

For Flow of hazardous substances in incineration residue in municipal solid waste incineration process, input is the amount of hazardous substances contained in the waste discarded into the incineration facilities, while output is mainly the amount of hazardous substances contained in emission gas, bottom ash, fly ash and waste water. Furthermore, when a melting facility is also installed in the incineration plant, output is the emission gas, melting fly ash, slag and waste water. Table 2 shows flow of Pb and PCDDs/DFs in the residue for waste incineration and ash melting when one ton of municipal solid waste is subjected to incineration. Here content of Pb and PCDDs/DFs in various residues is based on the average value in Table 1 from the viewpoint of total release of them. In the case of waste incineration, Pb total of 197g /ton-waste is released from bottom ash and fly ash. Even if this is melted, a total of 133g/ ton-waste is released from the slag and melting fly ash.

Table 3 Flow of Pb and PCDDs/DFs in the residues

Residue	**Residue released for one ton of waste (kg)**	**Pb content(ave.) (mg/kg)**	**PCDDs/DFs content(ave.) (ng-TEQ/g)**
Bottom ash	150	886	0.20
Fly ash	30	2150	6.54
Melting fly ash	4	28000	0.33
Slag	160	145	0.001

Residue	**Pb released for one ton of waste (g)**	**PCDDs/DFs released for one ton of waste (ƒ ĝ-TEQ)**
Bottom ash	132.9	30
Fly ash	64.5	196.2
Melting fly ash	112	1.32
Slag	23.2	0.16

Here the total release of Pb for one ton of municipal solid waste will be such that the release of bottom ash and fly ash added together should be almost the same as the release of the slag obtained by melting them and melting fly ash added together. This is because there is not much flow of Pb to emission gas and the metal. If they are different, this is because that part of bottom ash may contain fly ash. 65 g of Pb is present in the incineration fly ash for one ton of waste. When this is molten, 112g, about twice the weight, is concentrated in the melting fly ash, on the one hand. On the other hand, Pb present in the slag is much decreased. In the case of waste incineration, a total of 226 μg-TEQ of PCDDs/DFs is produced from bottom ash and fly ash. By contrast, when it is molten, a total of 1.48 μg-TEQ/ton-waste is produced from the slag and melting fly ash; namely, release is reduced by 99% or even more. For emission gas, the volume of generated emission gas in waste incineration is 5000 Nm^3/ton-waste. The concentration of PCDDs/DFs in the emission gas is 0.5 μg-TEQ/ton-waste when the emission standard of 0.1ng-TEQ/Nm^3 is assumed. It can be again confirmed that the residue accounts for a great percentage in the total release of PCDDs/DFs. It can be seen that treatment by melting is very effective to achieve the target value of 5 μg-TEQ/ton-waste [4) which is the target value of the total release of the PCDDs/DFs.

5. CONCLUSION

We have analyzed the content, leaching behavior and substance flow regarding the Pb and PCDDs/DFs contained in various types of incineration residue of municipal solid waste. This has led us to the following discovery:

1) The total release of Pb included in the residue from the municipal solid waste incineration facilities is 135 to 197g /ton-waste. Bottom ash accounts for about 67%, and fly ash occupies 33%. Furthermore, when melting is performed, the melting fly ash assumes 83 %, and slag 17%. The total release of PCDDs/DFs in the current form of the residue is about 227μg-TEQ/ton-waste. Fly ash account for about 87%, and bottom ash about 13%. When melting is performed, the total release is reduced by 99%.

2) Pb and PCDDs/DFs contents of almost all the fly ash exceeded the standard level (Pb: 600mg/kg, PCDDs/DF: 1ng-TEQ/g) involved in soil contamination. Pb leaching concentration was also high. Furthermore, the PCDDs/DFs content of melting fly ash is small, but Pb is concentrated to a higher level of concentration than that of fly ash. Fly ash are designated as general waste placed under special management in Japan at present. When disposing them, stabilization of heavy metals is required legally. It is hoped that these residues are subjected to PCDDs/DFs decomposition and recovery and recycling of heavy metals.

3) More than half of the Pb content and PCDDs/DFs content in bottom ash show the value below the standard level involved in above-mentioned soil contamination. Our study has suggested the possibility of making an effective use of them through adequate handling of ash, selection of the place of use and physical separation. However, bottom ash account for about 13% in terms of the total release of PCDDs/DFs from incineration facilities. Their reduction is expected.

4) The slag for which a guideline for effective use has already been specified shows the value much below the standard level involved in above-mentioned soil contamination, in terms of Pb content, PCDDs/DFs content and its leaching concentration. It is hoped that more active use of recycling will be promoted.

Subsequent task will be the study of factors having impact on PCDDs/DFs leaching, and acid neutralization capacity of residue affecting the leaching of heavy metals. It is also essential to make analytical studies centering on the flow of hazardous substances into the water system and their behavior. At the same time, it is important to examine the bottom ash for which possibility of recycling has been demonstrated, in an effort to clarify the difference of properties resulting from mixing them with other residues such as boiler ash, and to improve their properties through physical separating.

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Waste Materials in Construction
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New trends on EAF slags management in the Basque Country

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700,000 tonnes of primary slags are generated each year in the 13 steel plants located in the Basque Country, a small region of 20,664 Km^2. Nowadays, as there is not Spanish regulation concerning environmental aspects related to the utilization of wastes, this great amount of waste is being landfilled.

In order to solve environmental problems due to this kind of waste management a two years project covering the environmental aspects related to steel slags reutilization as a construction material was carried out. Results derived from the project have lead to a final draft of a Decree about steel slags reutilization as a construction material.

1. INTRODUCTION

13 steel plants in the Basque Country, a small region of 20.664 Km2, produce about 6,5 million tonnes of steel anually, this amount being 50% of the total production of Spain.
This production is focused on common and special steels that are processed by means of electric arc furnaces. The common steels are those composed of, basically, iron and carbon and the special steels are those that contain , apart from impurities and carbon, other voluntarily added alloys such as chromium, nickel, molybdenum, vanadium, wolfram etc.These alloying elements have a varied influence in the properties of the steels, as they may increase or decrease the hardness, machinability, etc.

As a consequence of the manufacturing of steel, some 700.000 tonnes of primary slags are produced each year. Currently, they are deposited either in the landfills owned by the companies responsible for their production, or in private or public landfills. It is thought that there may be non-controlled use of these wastes as they may be used as filling materials without the application of any environmental control.

This behaviour is against the current European environmental policies, which are focused on preventive measures (a decrease or minimization in the generated residues), and the recovery or reutilization of said residues. Such policies give dumping as the last alternative to be considered and only acceptable when it is carried out in proper environmental conditions and when no other possible alternative exists.

As a result of all this, and after having checked that no regulation existed in Spain with regard to environmental issues related to the slags, a two year long project was carried out in which the environmental and technical aspects related to the reuse of steel slags from the steel companies in the Basque country were analysed.

This project intended to develop an environmental management model for the reuse of the slags taking into account the environmental protection levels for the air, water and soil.

The results that were obtained have been used to formulate a Decree project concerning the reuse of the steel slags as materials for building applications and civil engineering.

2. METHODOLOGY

2.1 State of the art

A bibliographic study was carried out in order to know the regulations about environment criteria for the use of wastes in the building sector in several autonomous communities in our country, as well as other different European countries.

The references that could be found were:

- Orden de 15 de Febrero de 1996 sobre valorización de escorias (Catalonia) (1)

  It establishes the possibility of the use of the slags with the simultaneous analysis of the parameters involved in the leachate obtained and composition by means of easily conducted tests. This may imply a greater speed when the time to take a decision arrives.

  The established limits for the said parameters lack of well- founded technical reasons as they are the same which are established for the classification of the wastes as inert. Nevertheless the limitations and restrictions for their use are established so that the contact between the wastes and water is practically non-existent, thus avoiding the scattering of the contaminants present in the wastes into the existent aquifers

  It is centered on the use of the wastes as granular materials thereby leaving a void for its application in other fields.

- The Building Materials Decree (Netherlands) (2)

  The analysis of the feasibility of the use of the wastes and even the raw materials, must be made with a previous long and complicated methodology. This entails a good knowledge about the behaviour of the material but the decision on which material may be used or not is delayed.

  The environmental criterion in which it is based is centred on the acceptable changes in terms of soil composition and surface waters due to the dispersion of the contaminants present in the material.

- Construction materials decree (Belgium) (3)

  This decree is currently being evaluated. It is based on the same scientific-technical basis, protection criteria and laboratory tests as those used by the Dutch Decree. The following modifications are nevertheless incorporated:

  a) It allows the use of a waste whenever its composition or that of the material evaluated

with it don't surpass the reference values. In this case the decision is taken very quickly.
b) The limit values that are established for the case when the behaviour of the waste must be determined, that is to say, when the composition exceeds the reference values, are directly compared to the results of the test to be made (Tank test or column test). Even so, the time needed to take the decision continues to be long.

- Anforderungen an die stoffliche Verwertung von mineralischen reststoffen/Abfallen: Technische Regeln LAGA (Germany) (4)
  These technical rules give limit values for several determined elements but they are based on the knowledge of experts. A scientific basis is not given to prove the validity of the values. Hence values that are higher than those established as limit values are admitted whenever it is certified that no risk exists for the enviroment.

  On the other hand, and as in the Catalonian decree, it sets restrictions for their use so that the dispersion of the pollutant agent in the nearby aquifers is minimised, rendering it an acceptable risk for the environment.

The conclusion drawn from the different consultations made in other countries is that these materials are not used in the building industry, or, in the cases where they are used, its use is based on some of the described regulations or no limits are set for the environmental behaviour of the waste.

2.2 Model selection

As a result of the diversity in the criteria and limit values specified in the reference standards consulted, the need for developing a new specific standard for the slags generated in the CAPV (Basque country autonomuos community) was seen. The Dutch Decree "The Building Materials Decree" was used for that, since it is based on an environmental criterion based on scientific basis with well-founded reasoning that allows the transfer of the methodology to the particular case of the Basque Country.
It is worth mentioning that the said Decree asks for a rather strict demand level in terms of the environmental properties of the slags, due to the absence of soil and the low depth down to the phreatic level that exists in the reference country

2.3 Adaptation of the selected model to the case of the Basque Country

A methodology was proposed in order to adapt the selected model to the case of the Basque Country that was divided into two phases:

- Basis evaluation level or risk analysis: a thorough study of the features of the waste was to be made, so that the behaviour of the waste in the long term was known and the use conditions of the slags were established.

- Evaluation level related to the management or management model: taking into account that the objective was to determine, on an individual basis, the slags that were fit for use in the building industry, this level intended to establish a suitable methodology composed of a sampling methodology, the parameters to be determined, the limits for the parameters and the tests to be made.

2.3.1 Risk evaluation level

It was decided that the risk analysis related to the use of slags was made with the following two assumptions:

- The case in which the use entailed the incorporation of the slag into the composition of the soil.

The study was approached by means of the analysis of the composition of the slags and its comparison with the reference values of the Basque Country soils (5). The possibility of applying this methodology was defined for the cases in which the composition of the slags remained lower than the reference values.

This criterion agreed with the principles on which the policies of soil protection in our autonomous community are based, as well as those accepted by other countries such as Netherland.

- The case in which the use was carried out in a way that permitted that no slags were incorporated into the soil.

In these cases it was decided that an analysis on the long term environmental behaviour of the slags be made.

The methodology developed for this case was based on the Dutch Decree " The Building Decree".The main premise of this methodology was that, for each of the elements of interest of the slags, the contribution to the soil in a one hundred year period should not produce a change in the composition of more than 1% in the first metre of reference. In this case, it would be considered that the use of slags in touch with the soil presented an acceptable risk in environmental terms. Nevertheless, if the results were greater than the limit value, the establishment of an exhaustive study of the change that the use of the slags would entail in the composition of the soil and the risk that this change would suppose for the environment would be needed.

In the following paragraph a description of the steps taken to calculate the contribution of pollutants to the soil in a period of one hundred years is given, as well as the maximum values of that contribution for which the change in the composition of a reference soil may suppose a 1% value.

- Contribution to the soil of pollutants present in the slags in a one hundred period (inmission values).

In order to calculate the inmission values, the values of emission (release of contaminants present in the slags in a period of one hundred years) had to be calculated first. The key laboratory test to do that is the column test, that is valid for the determination of the leaching of the granular materials in liquid/solid ratio ranges of 0 and 10 ml/g. In this case it was needed to determine the release of pollutants in one hundred years and so it was necessary to establish the actual liquid/solid ratio that was reached in that period.

After having obtained the liquid/solid ratio in one hundred years and by fixing the results obtained in the column test, the release of pollutants for this ratio and for the liquid/solid ratio of ten was determined according to the fixing made and the factor that binds both values.

Once this factor was applied on the result obtained in the column test, for the liquid/solid ratio of ten, the release of pollutants corresponding to the period of one hundred years was obtained.
Complementary tests were carried out to correct the results due to the fact that the column test results are obtained in conditions in which the carbonation and oxidation reactions to which the slags are exposed in the Environment are not taken into account. pH static tests were carried out (to determine the influence of the pH in the leaching and correct the results of the column test) as well as availability tests (to define the correction factor due to the oxidation for the column test results).
These correction factors allowed a correction of the results obtained in the column test. In this way it was possible to calculate the release of the pollutants in the period of one hundred years, that is to say the release values.

Once this value was known, the expression for the calculation of the inmission values could be established:

$$I_{\text{slags}} = E^{L/S=10}_{\text{col.soils}} \bullet f^{\text{slags}}_{L/S} \bullet f^{\text{slags}}_{\text{pH}} \bullet f^{\text{slags}}_{\text{oxid.}} \bullet d_{\text{slags}} \bullet h_{\text{layer}}$$

Where:		
	I_{slags}	Contribution to the soil of pollutants present in the slag; in mg/m^2
	$E^{L/S=10}_{\text{col.soils}}$	Result of the column test, carried out on the soil, obtained for the liquid/solid ratio of ten; in mg/kg.
	d_{slags}	Apparent density of the slags; in kg/m^3
	h_{layer}	Height of the slag layers deposited in contact with the soil; in m.
	$f^{\text{slags}}_{L/S}$	Correction factor due to the difference between the liquid/solid ratio in 100 years and the liquid/solid ratio of ten in the column assay.
	$f^{\text{slags}}_{\text{pH}}$	Correction factor due to the change in the pH of leaching of the slags in the laboratory and in real conditions.
	$f^{\text{slags}}_{\text{oxid.}}$	Correction factor due to the oxidation that the soil undergoes when tested in the laboratory in real conditions.

Afterwards this expression was adjusted by subtracting from the inmission of the slags the inmission that the use of a natural granular soil would produce (in the cases when the thickness of the layer of the soil used was the same to that of the case of the slags).

The calculation of the release values of a natural soil was realized by the application of the same methodology used for the case of the slags (column test, adjusting functions, correction factors and calculation formula) to soils in which a significant human activity had taken place.

The creation of a soil is a natural process that takes thousands of years. This means that its chemical composition is stable enough as to consider that the carbonation and oxidation reactions due to the contact with the oxygen and carbon dioxide of the air be negligible. For this reason, the correcting factors due to the pH and the oxidation of the soil take values of one and they can be therefore deleted from the inmission calculation formula.

The same formula, with the addition of the density values belonging to the soil , used in the case of the slags was also used to obtain the liquid/solid ratio that was reached by the soil in one hundred years.
As a result of substracting the inmission of a natural soil to that of the slags the following expression was obtained:

$$I = (E^{L/S=10}_{col.slags} \bullet f^{slags}_{L/S} \bullet f^{slags}_{pH} \bullet f^{slags}_{oxid.} \bullet d_{slags} - E^{L/S=10}_{col.soils} \bullet f^{soils}_{L/S} \bullet d_{soil}) \bullet h_{layer}$$

- ➢ Contribution of the pollutants in the cases in which the change of the composition of the first metre of a reference soil is greater than 1% (maximum value of inmission).

The limit values that were used for checking the values obtained for the inmission were calculated with regard to the base criterion, that is to say, the limit was taken as the inmission or contribution that allowed a change in the composition of the first metre of a reference soil of the Basque autonomous community equal to 1%. In this way, the limit values were calculated according to the following formula:

$$I_{max} = \frac{\%}{100} \bullet V_{\cdot ref.} \bullet d_{soil} \bullet h_{prot.}$$

Where:	%	% maximum admissible change
	$V_{\cdot ref.}$	Reference value for the soils of the Basque autonomous community in mg/kg.
	d_{soil}	Density of the soil; in Kg/m3
	$h_{prot.}$	Height of the soil to be protected, in m.

2.3.2 Evaluation level related to the management or the management model.

The previously explained environmental study was too long as to be valid to separate the slags that could be used as granular materials in touch with the soil and the rest. This made necessary the development of a management model that permitted the realization of that task in a easy and simple way.

The leaching test described in the European Prestandard prEN 12457 (proceeding C) (6) was proposed as the management model to be applied over the sampled slags. This test was established with the work of specialists from several countries in the field of leaching tests and it consists of a two phase leaching with a total duration of 24 hours.
Once the test to be carried out had been defined, the calculation of the limit values was made according to the possible relation that may exist between the limit values that had been determined for the evaluation level (limit inmission values), and the results that were obtained from the proposed test. This task was carried out in two phases:
Phase 1: study of the relationship that exists between the maximum inmission values and the results with which they were related in the column test. It was obtained from the equation for the calculation of the inmission that took this form in the simplified state:

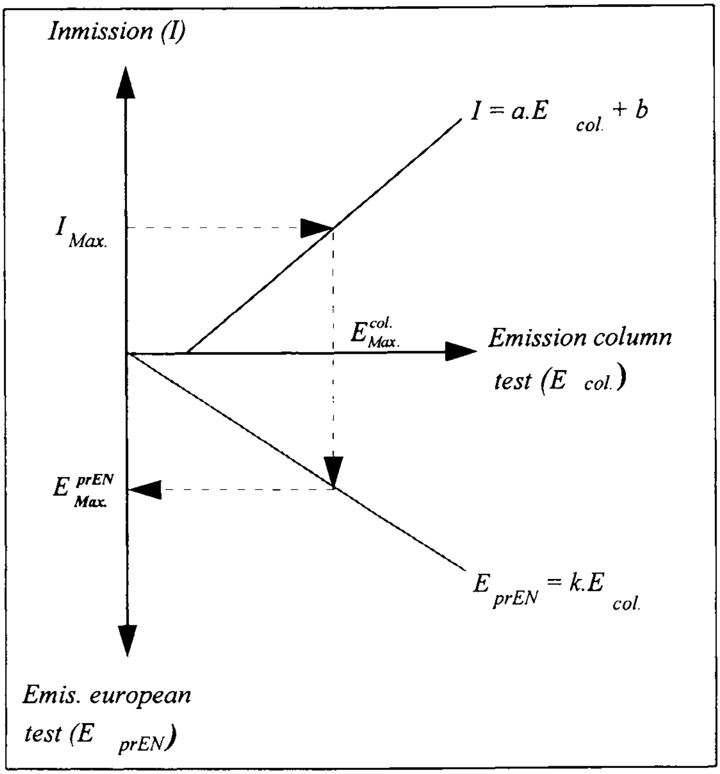
$$I = a \bullet E_{L/S=10}^{col.slags} + b$$

Phase 2: determination of the correlation that exists between the column test and the proposed European test, which was supposed to be adjusted to the expression

$$E_{prEN.slags} = k \bullet E_{col.slags},$$

it being necessary to determine the K constant for each element.

In this way and with the use of these two equations the limit value for the European test proposed was obtained. This can be represented in the following graphic:



2.3.3 Characterization test of the slags generated in the Basque Country

A detailed study of the slags of the Basque Country was carried out in order to be able to apply the mentioned methodology. To do this, several samples were taken from the eleven steel companies and they were all treated to obtain a unique slag sample. A sampling of different natural soils was also carried out according to the results of the study of the

reference level of the Basque Country. In this way the non- polluted state of the soils was guaranteed. These soils were later mixed and homogenized in order to make the test.
The study that was carried out was composed of the following tests:

- Physical tests
  Density: absolute density, real density and apparent density
  Porosity
- Chemical tests
  Chemical parameters: humidity, pH and free lime.
  Determination of the carbon and sulphur content, anions (fluorides, chlorides, bromides, sulphurs, sulphates and cyanides) and organic compounds (oils and greases, mineral oils, EOX content)
  Determination of the main components
  Determination of the trace elements
- X-Ray diffraction
- Leaching tests: DIN leaching test, column test according to the NEN standard 7343, test of availability according to the standard NEN 7341, test of oxidative availability, pH static test and leaching test according to the prestandard prEN 12457 (proceeding C)

3. RESULTS

3.1 Results of the application of the risk analysis to the slags created in the Basque country

- Case in which the use implied the incorporation of the slags into the composition of the soil.

When the reference values were compared to the composition of the slags, it was observed that the use of those wastes did not comply with level demanded, as can be seen in table 1:

Table 1
Composition of slags

Element	Slag 1	Slag 2	Slag3	Slag 4	Slag 5	Slag 6	Slag 7	Slag 8	Slag 9	Slag 0	Slag 11	Ref. V
As	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	23
Ba	374	741	1364	747	403	1008	1251	878	556	1706	807	150
Be	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	8
Cd	31	2,9	31	29	21	26	26	32	26	24	27	0,8
Co	7	10	4,9	5	6,8	22	7,5	5,5	4,8	4,2	5,6	20
Cr	3973	28630	8562	8425	6918	13904	7123	8699	13219	10137	9521	53
Cu	49	63	289	142	146	245	159	118	59	168	127	24
Hg	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	0,3
Mo	2,3	405	19	28	147	36	6,6	65	4,6	7,2	135	1,1
Ni	38	777	62	35	673	106	38	94	25	21	39	40
Pb	2576	87	4454	2271	1266	4891	3493	655	2445	2402	2620	40
Sb	12	<5	112	68	534	47	21	46	25	13	30	6
Se	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	0,25
Sn	6,2	5,8	10	9,7	8,7	12	9,5	4,5	2,1	5,9	2	0,1
Ti	3234	9222	2096	1497	1737	2096	4970	2036	2635	3174	2754	3600
V	503	503	726	447	447	615	838	726	1061	615	894	77
Zn	61	75	898	342	1368	149	95	156	62	172	89	106
F^-	728	18217	399	548	8261	438	940	656	749	7426	748	200

Table 1

Composition of slags

Element	Slag 1	Slag 2	Slag3	Slag 4	Slag 5	Slag 6	Slag 7	Slag 8	Slag 9	Slag 0	Slag 11	Ref. V
Br^-	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	1
SO_4^{2-}	3228	5311	2418	5169	10547	2899	3507	3811	2915	2983	4258	3282
CN^-	<0,005	<0,005	<0,005	<0,005	<0,005	<0,005	<0,005	<0,005	<0,005	<0.005	<0,005	0,1
Min. oil.	3	8	8	60	8	61	5	18	4	4	5	250
EOX mg Cl^-/kg	<0,05	0,2	1,8	<0,05	0,9	0,1	0,2	<0,05	0,1	<0.05	<0,05	4,5

Therefore, it was discarded as one of the possible uses of the slags.

- Case in which the use was carried out in conditions that did not imply the incorporation of the slags to the composition of the soils.

The values of the inmission of the slags corrected with the own inmission of the soil and the maximum inmission values are compared in table 2

Table 2

Comparison between the inmission of the slags and the maximum inmission values

Element	Slag 1	Slag 2	Slag3	Slag 4	Slag 5	Slag 6	Slag 7	Slag 8	Slag 9	Slag 0	Slag 11	Imax.
Al	59774	59774	32500	18862	179102	76821	70002	629136	83640	15453	138189	106500
As	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	345
Ba	131620	418005	12012	27173	79396	24646	<12854	81081	44019	17065	12012	2250
Be	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	120
Ca	4,1E+07	1,5E+07	5,3E+06	6E+06	2,5E+07	7E+06	3,3E+06	1,6E+07	9,2E+06	3,4E+06	4,3E+06	264000
Cd	<1,1	<1,1	<1,1	<1,1	<1,1	<1,1	<1,1	<1,1	<1,1	<1,1	<1,1	12
Co	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	300
Cr	269	1767	269	3077	269	3451	BIV	269	269	BIV	1205	795
Cu	BIV	BIV	BIV	BIV	29	BIV	BIV	BIV	BIV	BIV	BIV	360
Fe	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	487455
Hg	<4,8	<4,8	<4,8	<4,8	<4,8	<4,8	<4,8	<4,8	<4,8	<4,8	<4,8	4,5
K	11769	37059	97023	78773	136130	44880	14376	29237	3948	110059	3948	2340
Mg	<48553	<48553	<60495	<48553	<48553	<108263	<48553	<60495	<48553	60495	<132147	16770
Mn	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	15000
Mo	115	13275	1343	2366	3047	2025	320	1343	320	2706	18730	17
Na	88114	342043	45793	227170	354134	21609	63931	4076	33701	233216	94160	1380
Ni	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	600
Pb	BIV	42	BIV	BIV	4013	BIV	BIV	BIV	BIV	BIV	BIV	600
Sb	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	90
Se	<54	289	<54	<54	730	<54	<54	<54	<54	<54	<54	3,8
Sn	<79	<79	<79	<79	<79	<79	<79	<79	<79	<79	<79	1,5
Ti	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	54000
V	1136	597	11900	2481	463	6518	7863	2481	9209	10554	13246	1155
Zn	BIV	BIV	BIV	BIV	487	BIV	BIV	BIV	BIV	327	BIV	1590
F^-	BIV	24679	7159	421	26604	3501	1576	1768	BIV	11395	BIV	3000
Br^-	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	15
SO_4^{2-}	BIV	BIV	BIV	BIV	BIV	BIV	350323	32251	BIV	186073	120894	49230
CN^-	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	BIV	1,5

BIV: the inmission value of the slag is below the natural inmission of soils

The following points have to be made clear in order to make the analysis of these results:

- The aluminium, calcium, potasium and sodium are not considered harmful for the soil composition as they are already major components in its usual composition. Therefore, its determination into the management model is not considered of any interest.

- The tin is an accumulative element of the steel, that is to say, the slag is not able of retaining it.
- The mercury is a volatile element at the melting temperatures of the steel. In the case in which it is present in the raw materials used by the steel companies, it will not appear in the slags but in the produced dust.

The results showed that some elements such as barium, chromium, molybdenum, vanadium, fluor and sulphates were higher than the selected criterion (change of the soil composition of less than 1%) in a general way, and elements such as cadmium, nickel, lead, selenium and zinc could surpass them though in a one to one basis.

With the aim of making it possible for as great a number of slags as possible to be used in this application, a risk assessment was made in terms of human health and environment if increases greater than 1% were permitted for those elements that surpassed the established criterion in a generalised way.

The case of the sulphates needed a different approach due to the fact that the soil is not able to act as a filter for them and the leaching contents in the said anion directly increase the sulphate content of the underground waters.

It was concluded that changes in the soil composition higher than 1% for those compounds could be accepted with care as pointed out in the table 3:

Table 3

Accepted changes in the soil composition

Element	Ref. value mg/Kg	Final composition	Change %
Ba	150	255	70
Cr	53	55	4
Mo	1.1	4.4	300
V	77	86	12
F	200	212	6
Sulphates	64	67	5

In the case of the sulphates the reference value is that of the underground waters.

In the case of the chromium, which is a leachable element when it is in the oxided form, a change in the conditions of the steel manufacturing process by using less oxidizing conditions could decrease the amount of Chromium of this state and its effect on the soil could be diminished.

3.2 Results of the calculation of the limit values to be applied for the management model of the slags

After having defined these changes and limiting the change for the rest of the elements of interest in the 1%, the limit values to be applied in the leaching test prEN 12457 (proceeding C) were calculated for the elements that are defined in the table 4.

Table 4

Limit values to be applied in the leaching test prEN 12457

Element	Unit	Limit
Ba	mg/kg	17
Cd	mg/kg	0,009
Cr	mg/kg	2,6
Mo	mg/kg	1,3
Ni	mg/kg	0,8
Pb	mg/kg	0,8
Se	mg/kg	0,007
V	mg/kg	1,3
Zn	mg/kg	1,2
F^-	mg/kg	18
SO_4^{2-}	mg/kg	377

In the case in which the slags were to be used in rolling layers, it was deemed that the thickness of the layer that is in contact with the rainwater was 1 cm and the use of these slags was carried out by substituting the 100% of the aggregates used in the mixes. The propsed limit values are presented in table 5.

Table 5:

Limit values to be applied with slags used in rolling layers

Element	Unit	Limit
Cd	mg/kg	0,6
Se	mg/kg	0,2

4. CONCLUSIONS

The project carried out was useful for the determination of environmental aspects in the use of the slags of the Basque Country in the building industry and civil engineering and to create a management model to sort out the slags suitable for that use.

This model was used by the Basque government at the same time, to write one Decree proposal which regulates the validization and subsequent use of the slags that come from the production of slags in electric arc furnaces, in the frame of the Basque Autonomous Community.

The Decree proposal is being analyzed by steel makers, research centres, environment consultants and waste treatment companies and it will come for approval at the end on the present year.

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G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

The environmental quality of fly ashes from co-combustion

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In the Netherlands the government allows the co-combustion of maximum 10% of secondary fuels together with coal. To show whether the quality of fly ashes is affected by co-combustion, a broad research program was performed in which both the technical and the environmental quality of concrete with fly ashes from co-combustion were evaluated in comparison to the quality of concrete with reference fly ashes. In the research program fly ashes from co-combustion of sewage sludge, paper sludge, pet cokes, phosphorous gas, waste wood and a type of liquid hydrocarbon were evaluated. Both the technical and the environmental quality of most ashes from co combustion were shown to be comparable to that of regular fly ashes. This paper reports on the environmental quality of fly ashes from co-combustion; the technical quality is reported elsewhere (Lamers and Van den Berg, 1999). The leaching behaviour of concrete with fly ashes from co-combustion, is diffusion controlled. The components that were potentially introduced because of co-combustion did not lead to increase of leaching. As a result of the outcomes of the technical research program the Dutch regulations for fly ash as a filler or part of the binder were adjusted to make utilisation of fly ashes from co-combustion possible. Commercial operation of co combustion of several secondary fuels is running now at most of the Dutch coal fired power plants.

1. INTRODUCTION

Since 1995 Dutch coal fired power plants have considered the utilisation of secondary fuels in combination with hard coal. The economic advantages that arise from co-combustion of secondary fuels are large and they compensate possible drawbacks. An additional advantage is that the combustion of non fossil fuels leads to lower CO_2-emissions into the atmosphere. Until now the Dutch government allows maximum 10% co-combustion of secondary fuels. An extensive testing program has been carried out to test several types of secondary fuel in combination with hard coal. The following types of secondary fuels have been tested: dried sewage sludge, paper sludge, PET-cokes, phosphorous gas, wood and a liquid hydrocarbon.

From each of the test runs ash samples were selected. For every test mix coal – secondary fuel, minimum 3 days of operation was maintained to make sure that steady operation was reached. If possible also the reference fly ash was selected. This specific reference fly ash is a fly ash resulting from combustion of exactly the same coal mix in the same power plant in the same period, but without co-combustion of secondary fuel. Ash samples were always taken from a steady operation situation.

A prerequisite for co-combustion is that the extent of utilisation of fly ashes (and bottom ashes) is not reduced because of co-combustion. To accomplish this it was necessary to assess the suitability of fly ashes from co-combustion for utilisation as a construction raw material in cement and concrete, since cement replacement and use as a filler is one of the main markets for fly ash. Both the technical and the environmental quality had to be assessed. This paper focuses on the environmental quality of concrete with fly ashes from co-combustion. The technical quality of concrete with fly ashes from co-combustion is described in (Lamers and Van den Berg, 1999). A summary of the findings regarding the technical quality is given at the end of this paper.

A good environmental quality of concrete with fly ashes from co-combustion is a boundary condition for the effectuation of co-combustion and the verification of the technical behaviour. The diffusion behaviour of concrete with fly ashes from co-combustion was established and compared with that of concrete with reference fly ashes. In a BCR study (BCR, 1998; Hohberg et al., 1997) the diffusion behaviour of concrete with and without fly ashes was assessed by means of a tank leaching test based on the Dutch standard NEN 7345. The results showed that the leachability of components from concrete with regular coal fly ashes is comparable to concrete without fly ashes. Most components in the leachates did not exceed the detection limits.

The diffusion behaviour of concrete with fly ashes from co-combustion should be unchanged in comparison with regular fly ashes and should meet with the most stringent Dutch standards.

2. SAMPLE PREPARATION, TESTING PROCEDURES AND ANALYTICAL PROCEDURES

The leaching from concrete with coal fly ash, originating from co-combustion operations is compared with the leaching of concrete with reference coal fly ash. The reference coal fly ash has been formed in the same power plant, in the same period, using the same type of coal and firing conditions, but without co-combustion. The possible influence of the co-combustion on the leaching of concrete containing a specific type of coal fly ash (due to co-combustion) will be evaluated on that basis.

All types of fly ash were incorporated in standard concrete mixtures containing 340 kg/m^3 CEM I 32.5 cement, with replacement of 20% of the cement by fly ash. The water-cement ratio has been chosen in such a way that the slump is 70 mm. From this material concrete cubes were prepared, that were subjected to concrete technological tests, as well as to a leaching test according to the Dutch standard, NEN 7345. All types of fly ash conform to the concrete technological requirements of EN-450 for application of fly ash in concrete.

After 28 days of curing, the concrete cubes were subjected to a diffusion leaching test conform NEN 7345. In most cases a simplification of this test was applied: the separate fractions were mixed and analysed together. In this way, the leaching result can be considered as ε^*_{64d}, the measured cumulative leaching after 64 days. This simplification has been carried out, because it was assumed that the concentrations of most of the components would be lower than the corresponding detection limit, so that diffusion coefficients could only be calculated in an approximate manner. In the leachate resulting from NEN 7345 the concentrations of the components As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Sn, V, Zn and SO4 were analysed. Bromide, chloride and fluoride are hardly present in leachate from concrete; therefore, these components were not analysed.

For several types of concrete KEMA has performed complete diffusion leaching tests, i.e. with analysis of the separate fractions. The macro-elements, like Na, K, and Ca, in almost all cases showed diffusion controlled leaching. For the micro-elements, like As, Cd, Co, it was often not possible to demonstrate diffusion controlled leaching, because the concentrations in the leachate fractions were below the detection limits. These findings are in agreement with the conclusions of the most recent report in the framework of CEN (CEN, 1999). Therefore, for the interpretation of the leaching results discussed in the present report, it is assumed that the leaching of all relevant components is diffusion controlled.

All metal components were analysed by graphite furnace atomary absorbtion spectroscopy; sulphate was analysed by ion chromatography.

3. OVERVIEW LEACHING RESULTS, DISCUSSION PER SECONDARY FUEL

3.1 General introduction

In this chapter a description is given regarding the types of secondary fuel that are used for co-combustion. Under each paragraph a discussion is given of the specific co-combustion operation that is referred to, the influence of co-combustion on fly ash composition and a description of the relevant influences on leaching of concrete, compared to the reference fly ash.

All leaching results in this chapter are given in table 1; all results are given in units mg/m^2.

The results have been grouped according to the type of secondary fuel that is used for co-combustion. The co-combustion leaching results are every time compared to a reference, which is concrete with reference coal fly ash (not originating from co-combustion operations, but further from the same power plant, in the same period, from the same coal); these results are presented in table 1 as “0% (Ref)”. In some cases also results have been given for the leaching of concrete without fly ash; these results have been presented in table 1 as "100% cement". In figure 1 the average ratio for concrete leaching with / without co-combustion is shown. In figure 2 the average ratio between the leaching of concrete with fly ashes (both without and with co-combustion) and the Dutch Limit values is shown.

3.2 Co-combustion of pet-cokes

Petrochemical cokes (pet-cokes) is a residual product of oil refineries. The residue contains much carbon, as well as components from the crude oil, like sulphur, nickel and vanadium. During a co-combustion testing period performed at unit 9 of the Amer power plant in the Netherlands, two types of pet-cokes were co-fired, originating from two different refineries in the U.S.A.: Star Port Arthur (abbreviated as SP) and Shell Deerpark (SDP). The co-combustion percentage was 10%; the results have been encoded in the table as 10% SP, and 10% SDP, respectively. The reference coal fly ash has been encoded as 0% co-

combustion. As a result of the co-combustion of pet-cokes, the components molybdenum, nickel and vanadium are enriched in the fly ash.

From table 1 it is obvious that the leaching values for most of the components are below their detection limits. Only for barium, chromium, vanadium and sulphate measurable concentrations have been obtained. The leaching of chromium and vanadium slightly increases due to the co-combustion of 10% SP or 10% SDP. The concentrations of the elements molybdenum and nickel, which were enriched in the fly ash itself, are well below their detection limits in the leachate.

3.3 Co-combustion of dried sewage sludge

Dried sewage sludge has been co-fired in the power plant of Hemweg (unit 8) by the Dutch electricity producer UNA. The combustion experiments have been carried out using sludge dosages of 3% and 6%, as well as using coal without sludge (0%, (Ref)). The obtained coal fly ashes have been investigated for their chemical composition. Due to the co-combustion, copper, cadmium, lead and zinc are enriched by a factor 2 to 6 in the fly ash, in comparison with the reference coal fly ash.

In the leachate it was only possible to measure the concentrations of barium, cadmium, copper, lead, zinc and sulphate; for the other components, the concentrations were below the detection limit.

Special attention has been given to copper, lead, cadmium and zinc, since these elements are enriched in the fly ash due to the co-combustion of the sewage sludge. According to the results, incorporation of co-combustion fly ash in concrete has no influence on the leaching of copper from concrete. On the other hand, the leaching of cadmium, lead and zinc shows a slight increase when compared to the reference values. It is surprising that the leaching of these components is higher in the case of fly ash of 3% co-combustion than in the case of 6% co-combustion. A possible explanation for this phenomenon is that the enrichment of these components in the fly ash mainly takes place in the non-mobile fractions present in the fly ash.

3.4 Co-combustion of paper sludge

The Dutch electricity producer EPZ has co-fired paper sludge during a co-combustion testing period at the Amer power plant. The composition of this sludge is roughly 50% water, 25% cellulose fibers, 25% calcium carbonate and China Clay. The applied co-combustion percentages were 5% and 10%, respectively. Both the compositions of the macro-elements and the micro-elements in the resulting fly ash changed due to the co-combustion. The fly ash contains less SiO2 and more CaO than the reference fly ash. At a co-combustion percentage of 10% the contents of cadmium, mercury and zinc in the fly ash have increased to about 1.5 times the contents in the reference.

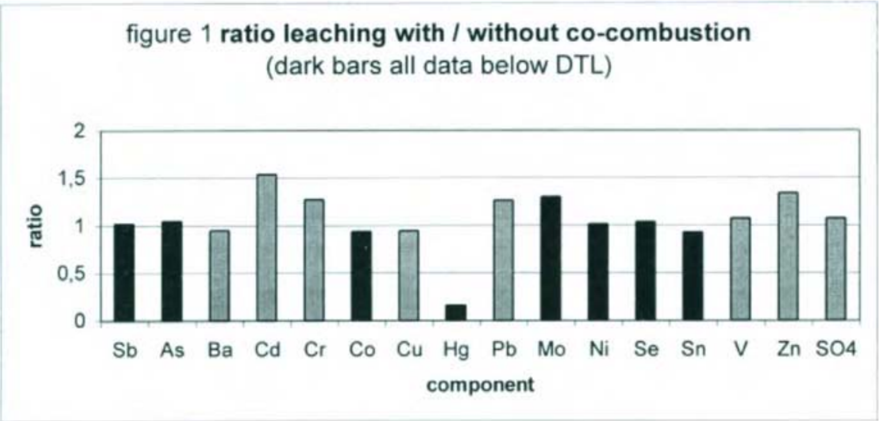
The codes that are used in table 1 are: 5%, 10%, and 0% (Ref).

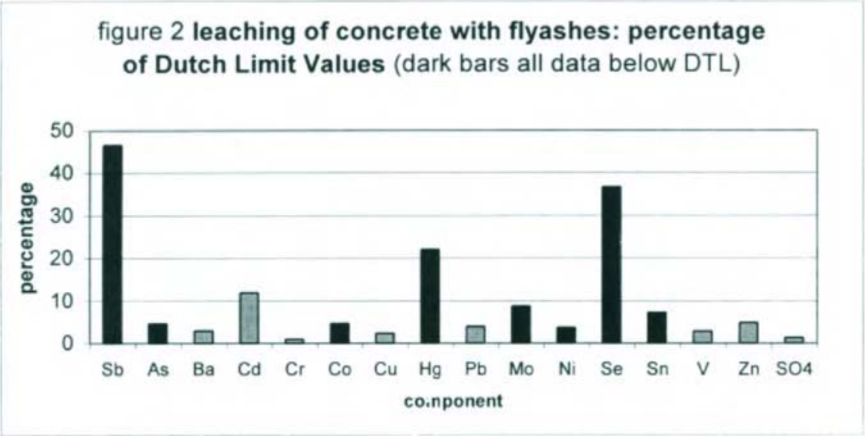
The concentrations of most components in the leachate are below the detection limits. This also applies to the enriched elements cadmium, mercury and zinc. Therefore, no conclusion can be drawn about the possible increase of the leaching of these components; however the leaching shows to be very low.

Table 1 leaching E 64d in the tank leaching test of components from concrete with fly ash from co-combustion of several types of secondary fuels, All results in (mg/m2). Only **fat results** exceed the detection limits (DTL); gray results below DTL. The Dutch limit values are printed in the last column; only if printed **fat**, the DTL has ever been exceeded

component	pet-cokes			concrete	sewage sludge					paper sludge		
	0% (Ref)	10% SP	10% SDP	100% cement	0% (Ref)	0% (Ref)	3%	3%	6%	0% (Ref)	5%	10%
Sb	< 2	< 2	< 2	< 1,6	< 1,6	< 1,6	< 1,6	< 1,6	< 1,6	< 1,9	< 1,9	< 1,9
As	< 2	< 2	< 2	< 1,6	< 1,6	< 1,6	< 1,6	< 1,6	< 1,6	< 1,9	< 1,9	< 1,9
Ba	**14,3**	**14,5**	**16,1**	**35,9**	**15,7**	**39,3**	**35,3**	**19,3**	**11**	**23,2**	**21,6**	**29,1**
Cd	< 0,07	< 0,07	< 0,07	**0,25**	**0,13**	**0,14**	**0,64**	**0,64**	< 0,07	< 0,05	< 0,05	< 0,05
Cr	**0,93**	**1,06**	**4,3**	**0,8**	**1,3**	**0,7**	**1**	**0,9**	**1,1**	< 1,3	< 1,3	< 1,3
Co	< 1,0	< 1,0	< 1,0	< 2	< 2	< 2	< 2	< 2	< 2	< 1,3	< 1,3	< 1,3
Cu	< 1,0	< 1,0	< 1,0	**1,6**	**1,4**	**1,4**	**1,3**	**1,5**	**1,3**	< 1,3	< 1,3	< 1,3
Hg	< 1,0	< 0,02	< 0,02	< 0,07	< 0,07	< 0,07	< 0,07	< 0,07	< 0,07	< 0,02	< 0,02	< 0,02
Pb	< 1,3	< 1,3	< 1,3	**8,4**	**8,7**	**10,1**	**13,5**	**21,5**	**9,1**	< 1,1	< 1,1	**1,8**
Mo	< 0,02	< 1,5	< 1,5	< 1,3	< 1,3	< 1,3	< 1,3	< 1,3	< 1,3	< 1,0	< 1,0	< 1,0
Ni	< 1,5	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Se	< 0,1	< 0,2	< 0,2	< 0,27	< 0,27	**0,61**	< 0,27	< 0,27	< 0,27	< 0,2	< 0,2	< 0,2
Sn	< 1,6	< 1,6	< 1,6	< 3,3	< 1,3	< 1,3	< 1,3	< 1,3	< 1,3	< 3,3	< 3,3	< 3,3
V	**5,3**	**8**	**6**	< 6,7	< 6,7	< 6,7	< 6,7	< 6,7	< 6,7	**6,7**	**6,7**	< 6
Zn	< 6	< 6	< 6	**11,3**	**11,3**	**9,8**	**35,9**	**27,9**	**8,5**	< 6	< 6	< 6
SO4	**320**	**340**	**350**	**400**	**485**	**320**	**730**	**340**	**305**	< 133	< 133	< 133

component	concrete	wood			Liq, HCH	phosporous gas			Dutch limit values Cat, 1
	100% cement	0% (Ref)	1,70%	3,60%	1,50%	0% (Ref)	3,30%	5,80%	
Sb	< 1,6	< 1,6	< 1,6	< 1,6	< 2,00	< 1,5	< 1,5	< 1,5	3,7
As	< 2	< 2	< 2	< 2	< 2,66	<2	<2	<2	41
Ba	**12,6**	**8,4**	**10,1**	**5,3**	**28,6**	**12,2**	**8,1**	**9,3**	**600**
Cd	< 0,05	< 0,05	< 0,05	< 0,05	< 0,064	< 0,06	< 0,06	< 0,06	**1,1**
Cr	< 2	< 2	< 2	< 2	< 1,33	**0,7**	**0,8**	**0,8**	**140**
Co	< 1,0	< 1,0	< 1,0	< 1,0	< 1,00	< 1,0	< 1,0	< 1,0	29
Cu	< 1,3	< 1,3	< 1,3	< 1,3	< 1,06	< 1,0	< 1,0	< 1,0	**51**
Hg	< 0,02	< 0,02	< 0,02	<0,02	< 0,016	< 0,02	< 0,02	< 0,02	0,4
Pb	< 1,9	< 1,9	< 1,9	< 1,9	< 1,52	< 1,8	< 1,8	< 1,8	**120**
Mo	< 1,3	< 1,3	< 1,3	< 1,3	< 2,00	< 1,2	< 1,2	< 1,2	14
Ni	< 1,3	< 1,3	< 1,3	< 1,3	< 1,33	< 2	< 2	< 2	50
Se	< 1,9	< 1,9	< 1,9	< 1,9	< 0,264	< 0,17	< 0,17	< 0,17	**1,4**
Sn	< 1,6	< 1,6	< 1,6	< 1,6	< 3,32	< 2,7	< 2,7	< 2,7	29
V	**6**	**6,7**	**8**	**8**	< 6,7	**5,3**	**4,7**	**6**	**230**
Zn	< 6,7	< 6,7	< 6,7	< 6,7	< 5,3	< 6,7	< 6,7	< 6,7	**200**
SO4	393	600	580	700	562	187	193	187	**27000**





3.5 Co-combustion of wood

The Dutch electricity producer EPON has performed co-combustion experiments using wood in the power plant near Nijmegen. The combustion operations were performed using 100% coal (encoded as "0%, (Ref)"), 600 kg of coal with 10 kg of wood ("1.7%"), and 280 kg of coal with 10 kg of wood ("3,6%").

Apart from the concrete cubes with the fly ashes (0%, 1,7% and 3,6%), a concrete cube without fly ash (100% cement) was tested as well..

Table 1 shows that the leaching from 100% concrete (without fly ash) is comparable for all components to the leaching of concrete with 20% coal fly ash (0%, (Ref)), while most leaching results are below their detection limits. This conclusion is in good agreement with the findings in the framework of CEN.

The incorporation in concrete of coal fly ash that was formed during the co-combustion of wood has no measurable effect on the leaching behaviour: the results are almost identical to the leaching values for 100% cement and for concrete with reference coal fly ash. Special attention was given to the elements that are enriched in coal fly ash due to the co-combustion of wood, such as cadmium, chromium, lead and zinc. The leaching of these elements has been below the detection limits in all cases. This means that no conclusion can be drawn concerning the possible increase in leaching due to the enrichment; in any case, the leaching is very low.

3.6 Co-combustion of liquid hydrocarbons

EZH, a Dutch electricity producer, has performed a series of co-combustion experiments in the Maasvlakte power plant, using so called arcru-bottoms as 1.5% co-firing fuel. ARCRU-bottom is a liquid hydrocarbon, formed as a residual product from the recovery of molybdenum from process streams, produced by ARCO-Chemie Nederland B.V. The coal fly ash which is formed during the co-combustion is enriched mainly in molybdenum.

Concrete cubes have been prepared using the coal fly ash from the co-combustion operation only. In this case no reference coal fly ash was tested, since the main goal of the leaching experiments was to check whether the leaching values were below the emission limiting values, as imposed by the Dutch government (all leaching results were far below these limiting values).

The leaching of concrete containing coal fly ash from co-combustion of ARCRU-bottoms, does not show significant increases with respect to leaching values of reference coal fly ash from the other series described in this report. The leaching of molybdenum is still below the detection limit, which means that it is not possible to draw any conclusion about the effect of co-combustion of ARCRU-bottoms on the leaching behaviour of molybdenum. In any case, the leaching is very low.

3.7 Co-combustion of gas from phosphorous ovens

Gas from phosphorous ovens, a residual product from Hoechst Holland B.V., was co-fired in unit 12 of the Dutch power plant in Borssele. Experiments showed that only the content of P2O5 in the resulting fly ash increases due to the co-combustion, while the micro-composition hardly changed. Co-combustion percentages were 3.3% and 5.8%, respectively (these are also the codes used in table 1).

In the leachates from the diffusion test NEN 7345 the concentrations of most components were below their detection limits, except for barium, chromium, vanadium and sulphate. However, the leaching of these components does not increase due to the co-combustion.

3.8 Discussion

The results described in this report were obtained by application of the Dutch standardized diffusion leaching test (NEN 7345). However, in contrast with this standard, during the experiments the leachate fractions were not analysed separately but mixed together. It was assumed beforehand that the leachate concentrations of most components would be below the respective analysis detection limits. The detection limits were taken as "maximum leaching" in these cases, while the real leaching values probably will be (much) lower. Application of the "complete" diffusion test for the present situations would have meant a large amount of analyses with only a small amount of useful results.

Since the separate leachate fractions were analysed together, it is not possible to prove that the leaching behaviour of components of concrete with 20% coal fly ash (from co-combustion operations) is controlled by a diffusion mechanism. However, KEMA has shown frequently by means of experiments that diffusion controlled leaching does take place for several types of concrete, including concrete containing 20% "normal" coal fly ash (KEMA, 1996). Therefore, the assumption that diffusion controlled leaching takes place in the cases described in this report is a reasonable one. This assumption is also in agreement with the findings that have been reported in the framework of CEN (BCR, 1997; CEN, 1999). The experiments directly result in values for the measured cumulative leaching after 64 days, ε*64d. These values serve as good measures for the determination of the ecological quality of concrete with coal fly ash (originating from co-combustion operations), with respect to leaching.

The following results were found regarding leaching from concrete with fly ash, both with and without co-combustion of secondary fuels.

- the concentrations in the leachate of the components As, Co, Hg, Mo, Ni, Sb, Sn were always below the analysis detection limit
- the concentrations in the leachate of the components Cr, Cu and V partly were below the detection limit and partly exceeded the analytical detection limit; in that case the concentrations were however very close to the detection limit
- the concentration of the component Se only in one case exceeded the detection limit
- the concentrations of Cd, Pb and Zn only exceeded the detection limits for the concrete samples from the series “co combustion of sewage sludge”. Although 3% co-combustion led to a significant increase of the concentration, also samples with 100% cement and “0% (Ref) exceeded the detection limits and showed significantly higher concentrations than in other series
- only for the components Ba and SO4 in all concrete samples concentrations could be measured.

When the leaching results, expressed in mg/m2 are compared with the most strict emission limit values from the Dutch Building Materials Decree (see table 1), in no case these limit values were approached.

The leaching of components of concrete containing reference coal fly ash is generally very low, which is shown by the values in table1 under "0% (Ref)”.

Coal fly ash which is formed during co-combustion operations often contains a higher concentration of one or several components, depending on the type of "fuel" that is used for the co-combustion. When this co-combustion fly ash is incorporated in concrete, the leaching results for the components from this concrete can follow one of the scenario’s mentioned below, in comparison to concrete with reference coal fly ash:

- the leaching is still below the detection limit; no conclusion can be drawn on the possible occurrence of an increase in leaching. This result has been found for most of the leaching values described in this report. The use of these types of fly ash in concrete will give no deterioration of the ecological quality of the concrete with respect to leaching, since the leaching is not detectable
- the leaching is above the detection limit, but does not increase due to the co-combustion operation (for example copper in the case of sewage sludge). This means that the increased content of this component will be mainly present in the non-available fractions. These types of coal fly ash will not deteriorate the ecological quality either

- the leaching increases due to the co-combustion, but is far below the limiting values imposed by the government (eg chromium in the case of pet-cokes, or lead and zinc in the case of sewage sludge). These types of fly ash can be incorporated in concrete without any problems concerning leaching
- the leaching increases due to the co-combustion, in such a way that it may be considered as a critical element (for example cadmium in the case of sewage sludge for the Dutch situation; the leaching is at its maximum still 50% below the stringent Dutch emission limiting value). These types of fly ash still can be incorporated in concrete, but it is advisable to check the leaching on a regular basis.

All types of concrete containing coal fly ash (with and without co-combustion) that have been described in this report, can be applied as construction materials without any objections concerning leaching, without the necessity of isolation measures, and even in permanent contact with ground water or surface water. The leaching values of concrete with coal fly ash, originating from co-combustion operations, are in all cases almost identical to the leaching values of concrete with reference coal fly ash, despite the enrichment of some components in the fly ash due to the co-combustion.

4. SUMMARY OF THE TECHNICAL QUALITY OF FLY ASHES FROM CO-COMBUSTION

The technical procedure that was followed for the assessment of the suitability of ashes from co-combustion for use as a filler and cement replacement consisted of the following parts:

- assessment whether the existing standards for fly ash for use in concrete can be met for fly ashes from co-combustion. This assessment has been closed with a positive answer
- execution of durability tests and tests regarding the action of cement chemicals, with the purpose to get an indication whether fly ashes from co-combustion show differences from conventional fly ashes in that respect.
  The test results showed no significant differences between fly ashes from co-combustion and their reference fly ashes (fly ashes from combustion of the same coal blend in the same power plant but without co-combustion). From the experience that was gained during this part of the program, it was established that only a part of the tests that were executed are necessary for future characterisation of an unknown fly ash from co-combustion:
- for durability testing only testing of the chloride-penetration and the frost-thaw salt resistance is necessary
- For testing of the action of (super)plasticisers only one type of plasticiser needs to be used.

Based on the results of the project the Dutch standardisation agency for construction has formulated a procedure to allow the utilisation of fly ash from co-combustion as a regular fly ash (CUR 1999). Through a non-recurrent testing program it should be shown that the durability properties and the action of cement and concrete chemicals is comparable to that of regular fly ashes without co-combustion and that the demands from EN 450 are met. If the allowance program is passed, fly ashes from co-combustion are shown to be conform with other fly ashes and they are sold to the market as regular coal fly ashes.

5. CONCLUSIONS

Incorporation in concrete of coal fly ash, which is formed during co-combustion of pet-cokes, has only a very small effect on the quality of the concrete with respect to leaching: the leaching of chromium and vanadium increases very slightly due to the co-combustion. However, this increase is only marginal.

Coal fly ash that originates from the co-combustion of sewage sludge, is enriched in cadmium, copper, lead and zinc compared with the reference coal fly ash. Upon incorporation in concrete, the leaching of copper does not increase, while the leaching of cadmium, lead and zinc does. This increase is only marginal for lead and zinc, compared to Dutch immission limiting values. For the co-combustion conditions described here, the leaching of cadmium increases to about 50% of the stringent emission-limiting value that is imposed by the Dutch government. This 50% increase is only the case for 3% co-combustion; at 6% co-combustion there is no increase in leaching with respect to the reference. According to this Dutch standard, concrete containing this type of coal fly ash can still be used for all construction purposes without any problems. However, in the case of co-combustion of sewage sludge, it is advisable to check the leaching of cadmium on a regular basis.

Co-combustion of paper sludge, wood, ARCRU-bottoms and gas from phosphorous ovens has no effect or only a very slight, negligible, effect on the leaching of components of concrete containing these co-combustion coal fly ash types.

The application of coal fly ash, originating from the co-combustion operations described in this report, does not lead to a significant change of the leaching behaviour of concrete, when compared to the application of coal fly ash which is formed during "normal" coal combustion (i.e. without co-combustion). These types of coal co-combustion fly ash can be applied without any ecological objection to the preparation of concrete, which is to comply with the most stringent Dutch requirements for construction materials.

A good environmental quality of concrete with fly ashes from co-combustion is a boundary condition for the effectuation of co-combustion and the verification of the technical behaviour.

A procedure was developed to show that fly ashes from co-combustion (maximum 10% of co-combustion) are technically equal to fly ashes without co-combustion. This procedure consists of the tests of the EN 450 standard extended with a "conformity analysis", in which the effects of the fly ashes from co-combustion on durability and on the action of cement additives are established. This procedure has been made part of the Dutch technical standards (CUR, 1999).

A series of fly ashes from co-combustion were technically assessed: They met the demands from the EN 450 standard and also showed to be conformous to fly ashes without co-combustion. Because the utilisation of fly ashes from co-combustion is safeguarded, the road is made free for large scale co-combustion of secondary fuels. All the Dutch coal fired power plants are now successfully co-firing on a large scale, thus reducing their operational costs and contributing to a reduction of CO2 –emissions.

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A Dynamic Approach to the Assessment of Leaching Behavior

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This paper describes a set of experiments that were used to investigate the mechanisms that control the rate of leaching from municipal solid waste incinerator ashes and a numerical approach to the estimation of mass transfer coefficients. A small column reactor was used for the experiments, and chemical equilibrium speciation software was used to assist in analyzing the leachate composition. It was found that certain major ions and trace metals were limited by the solubility of various solid phases, while other major ions were limited in concentration by physical transport processes. The numerical model was able to satisfactorily predict the influence of the controlling solid phases, and was able to estimate the governing mass transfer coefficients. For example, the model accurately predicts that the release of lead from the ash is controlled early on (the first approximately 50 pore volumes) by the solubility of $PbSO_{4(s)}$, and for the following approximately 3000 pore volumes was controlled by the solubility of $Pb(OH)_{2(s)}$. Effective diffusion coefficients were significantly lower for trace metals and reactive major ions than for salts, indicating sorptive retardation within the ash matrix may be occurring.

1. INTRODUCTION

In the United States, approximately 17% of municipal solid waste (MSW) is incinerated each year (EPA, 1998). This amounts to approximately 36 million tons, which generates approximately 7.2 million tons of residue that must be managed. In the United States, some 94% of MSW combustion residue is disposed of, while 6% is reused in a beneficial way (most of this 6% is used in the landfill environment, however, typically as landfill cover) (Wiles, 1999). Many European countries reuse as much as 90% of ash from MSW combustion (Wiles, 1999). Several demonstration projects in the US have been completed, and focused on the use of bottom ash in construction applications, primarily as aggregate substitute in asphalt or concrete or as a road base aggregate substitute (Eighmy et al., 1996; Demars et al., 1993; Hooper, 1991; Wiles, 1999).

Far fewer reuse options are available for residue collected from combustion pollution control devices, typically referred to as MSW fly ash. MSW fly ash can be extremely soluble (up to 30% in some cases), and in addition contains much higher concentrations of heavy metals that may pose an exposure threat and typically result in the ash being classified hazardous based on its toxicity characteristic (Theis and Gardner, 1990).

The potential for hazardous components to leach from the ash is a concern whether it is being reused or placed in a disposed environment. Furthermore, the experimental or theoretical determination of what concentrations will be leached under a particular set of environmental conditions remains elusive. The present methods that exist for the evaluation of leachate composition and properties rely primarily on static batch extraction techniques (e.g. the Toxicity Characteristic Leaching Procedure, the EPA Extraction Procedure). Also used to a lesser extent are large-scale dynamic lysimeters, placed either in the laboratory or in the field, which attempt to simulate the disposal environment. Static batch extraction techniques are useful in determining the elemental composition of ashes, equilibrium pH, and the major ions present, but may yield relatively little data concerning leachate quality under environmental conditions. The large lysimeters are able to simulate environmental conditions more effectively, but can be costly and time-consuming to run. A number of researchers have also employed serial batch extractions that attempt to simulate conditions in a column or in the natural environment (e.g. Eighmy, 1995; B≅verman et al., 1997).

This study used small column reactors to investigate the leaching behavior of municipal solid waste incinerator ash, and focused on the experimental determination of mechanisms that limit the concentration of major ions and trace metals in a dynamic leaching environment. The advantages of using this type of reactor include the ability to manipulate experimental conditions, such as flow rate, which permits discrimination of the controlling physical and chemical processes. This type of information regarding the underlying mechanisms that control leaching is transferable to a different environment using an appropriate modelling approach.

The experimental results from this study are interpreted with a chemical speciation model and further with a dynamic multi-component transport model. The dynamic model was developed to estimate those parameters which govern the composition of leachates from ash materials. This model is capable of using the experimental solute release data from the column experiments to estimate the governing coefficients, and subsequently to describe solute release subject to physical (diffusion) and chemical (precipitation) controls.

2. MATERIALS AND METHODS

2.1 Sample Collection

Twelve ash samples were collected from six different incinerators; the results presented in this paper will be restricted to a MSW fly ash collected from a starved air incinerator with a capacity of 50 tons per day. The samples were prepared by drying at 103°C before all analyses and experiments.

2.2 Chemical Analysis

Trace elements were analyzed using atomic absorption spectrophotometry (Perkin-Elmer Zeeman/5000 system). Both flame and flameless methods were used, with matrix modification as specified by the manufacturer. Major Ions (Ca, Mg, Na, K, Cl, $S0_4$) were analyzed by ion chromatography interfaced with an integrator (Dionex 4000i/4270).

2.3 Experiments

The mini columns used in this research have an inside diameter of 1.5 cm and a variable length up to 5 cm, yielding a maximum sample volume of approximately 8.8 cm^3. Samples were retained in the column by 0.45 μm cellulose acetate filters backed by glass fiber filters. Effluent from the column passed through two small-volume flow-through cells, one containing a pH probe, the other an oxidation-reduction potential probe. Finally, effluent was collected in a fraction collector in 20 ml volumes (approximately 40 pore volumes, which was the minimum volume required for all major ion and trace metal analyses).

The samples collected from the fraction collector were split into two parts. One was preserved with 0.2% $HN0_3$, and one was left unpreserved. The samples were all stored at 4°C for subsequent analysis.

Column experiments were conducted at four different flow rates: 0.1, 0.5, 2.0, and 6.0 ml/min (corresponding to Darcy velocities of 0.057, 0.283, 1.13, and 3.4 cm/min). The duration of the experiments varied between 115 and 220 hours.

3. RESULTS AND DISCUSSION

The pH was continuously monitored in the effluent from the column using small volume flow-through reactors. Figure 1 shows the pH behavior as a function of the pore volumes passed through the column for the four flow rates. Figure 1a provides a detailed view of the first 2,500 pore volumes of leachate, while Figure 1b demonstrates the longer-term trends (up to approximately 90,000 pore volumes for the highest flow rate experiment). All of the ash samples show similar trends in pH, which rises from the neutral or acidic range (4.5-6.5) into the basic range (10-11).

The low pH at the beginning of leaching is assumed to be due to acid aerosols (such as HCl and H_2SO_4) which are condensed on the surface of the particles as cooling occurs. Since these acidic components have the lowest condensation temperature in comparison with metal vapors, they are the last to condense and, conversely, among the first to leach into solution. The subsequent rise in pH reflects the dissolution of more basic components from the ash surface, the majority of which are from the addition of bases to control acidity and corrosion in the combustion chamber. The equilibrium pH determined using batch tests for this ash material was approximately 6.5 for a wide range of liquid/solid ratios.

Figure 1a demonstrates that the pH of the effluent solution is a function of the velocity of the solution through the ash bed. Slower flow rates experience a significantly higher solution pH, and decrease toward neutrality more rapidly as well (in non-dimensional time as represented by pore volumes). In real time, of course, the slowest flow rate would take much longer to return to the neutral pH range than would the highest flow rate (referring to Figure 1b, the slowest flow rate experiment was actually run for the shortest period of time).

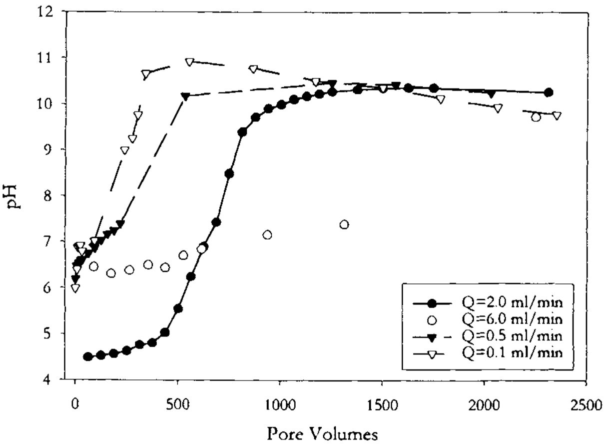

Figure 1a pH as a function of time (represented non-dimensionally as pore volumes): first 2,500 pore volumes.

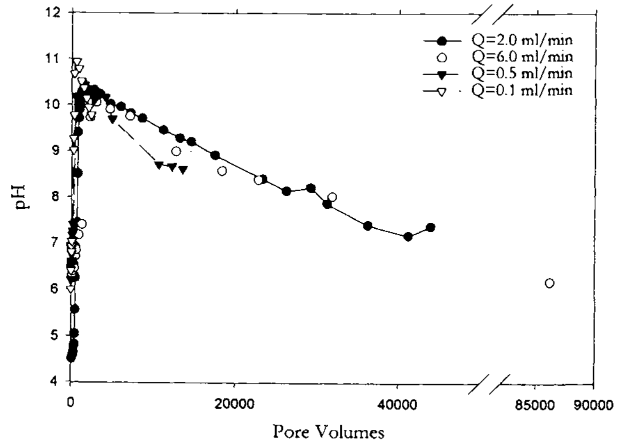

Figure 1b pH as a function of time (represented non-dimensionally as pore volumes): entire experiment length.

3.1 Element Release

Two phenomena can be demonstrated by inspection of the leaching curves. First, the rate of leaching of many strong base and strong acid ions was controlled by mass transfer processes, and second, the concentrations of certain major ions and trace elements in the leachate were controlled by the solubility of various solid phases. Figure 2 demonstrates the leaching behavior of a strong base cation, in this case potassium, at three different flow rates. As would be expected with no solubility controls, the potassium concentration in solution increases in response to increased contact time in the ash bed. The quasi-steady state concentrations in the figure are 6.5 ppm, 11 ppm, and 60 ppm for 2.0, 0.5, and 0.1 ml/min flow rates, respectively.

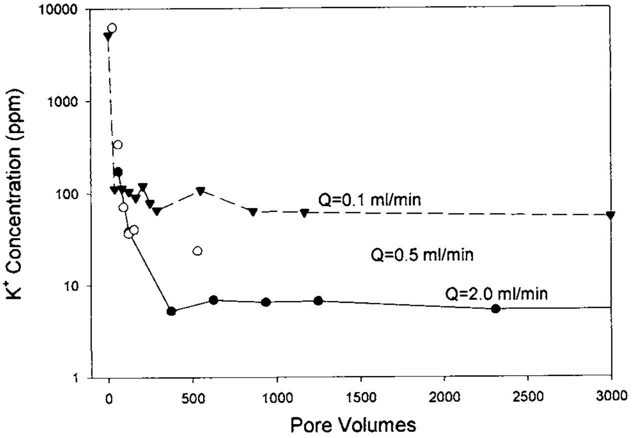

Figure 2 Concentration of potassium in leachate at three different flow rates.

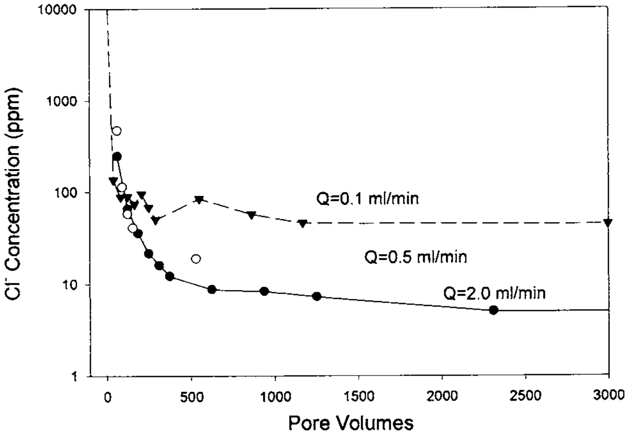

Figure 3 Concentration of chloride in leachate at three different flow rates.

A similar trend is observed with chloride, as shown in Figure 3. Again, concentration increases as the time available for diffusive transport from the ash surface and from within the ash matrix is increased. The quasi-steady state chloride concentrations in Figure 3 are approximately 5 ppm, 10 ppm, and 45 ppm for 2.0, 0.5, and 0.1 ml/min flow rates.

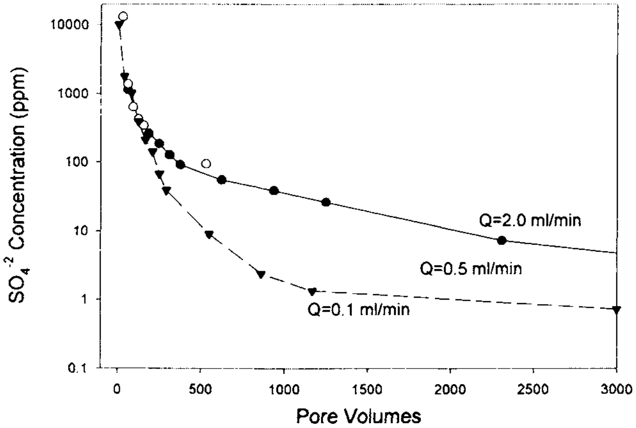

Figure 4 Concentration of sulfate in leachate at three different flow rates.

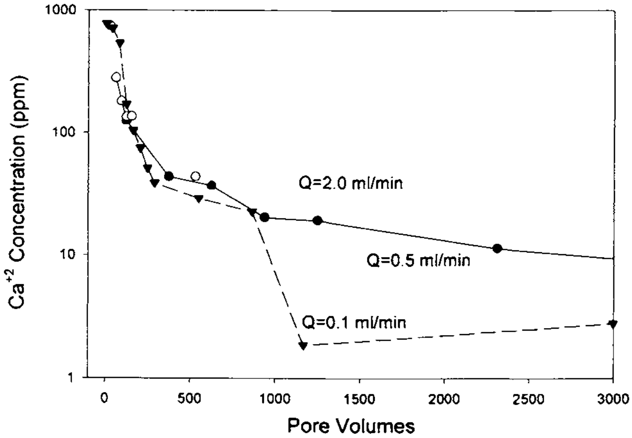

Figure 5 Concentration of calcium in leachate at three different flow rates.

The leaching behaviors of the trace elements and calcium and sulfate are distinctly different from the salts above. Figure 4 shows the leaching curves for sulfate at the three different flow rates. Although the concentration profiles are not identical for the three flow rates, they are similar and, moreover, the order of the curves is reversed from that seen with the conservative elements. That is, the leachate generated at the lowest flow rate has the lowest concentration of sulfate. Figure 5 demonstrates very similar behavior for calcium: similar concentration profiles among the three flow rates early in the leaching process and a reversal of the curves (relative to that seen above) at longer times. It is likely that the differences in pH is one cause of the differences of $[Ca^{+2}]$ and $[SO_4^{-2}]$ observed between the different flow rates (the lower flow rates have a higher peak pH at earlier non-dimensional times and lower pH at later times). It is also possible that the formation of certain solid phases is kinetically limited, and have a longer time to equilibrate in the experiments with lower flow rates. Nevertheless, the concentration differences are much less pronounced than with the conservative components of the leachate.

The chemical composition of the solutions was investigated using the equilibrium speciation program HYDRAQL (Papelis et al., 1988), which was employed as a tool to generate ion activities in the leachate. The results of activity determinations were interpreted as demonstrated in Figure 6a for data from the Q=0.1 ml/min experiment. Here the log of Pb^{+2} activity is plotted against $p(SO_4^{-2})$, where (SO_4^{-2}) represents sulfate activity. The solid lines in the figure represent the range of solubility values found in the literature for $PbSO_4(s)$. It should be kept in mind that this series of plots have a third dimension, time. The sulfate values display a relatively simple decay-type curve (see Figure 4), so that the time line in Figure 6a is left to right, that is, decreasing sulfate corresponds to increasing time. It appears that the first data point falls within the solubility envelope for $PbSO_4(s)$ and after the first three data points all subsequent values fall well below the solubility limit. In comparison, Figure 6b shows log (Pb^{+2}) vs. pH and is compared with the theoretical solubility of $Pb(OH)_2(s)$. The first three data points, those that are potentially in equilibrium with lead sulfate, are undersaturated with respect to lead hydroxide due to the low pH during early times. As the pH rises and SO_4^{-2} activity decreases, it appears that lead activity in solution is controlled by the solubility of lead hydroxide. It is also interesting to note the time sequencing of the data points in Figure 6b. As shown in Figure 1, the pH starts at a low value, reaches a maximum, and subsequently drops toward neutrality. The data points in Figure 6b, then, start at the far left, proceed to a maximum pH, and return toward the left, while following the $Pb(OH)_2(s)$ solubility line. At the peak pH values carbonate activity reaches a maximum, and the lead activity may be temporarily controlled by the solubility of $PbCO_3(s)$ (graphical representation not shown). Lead activity, then, does not display simple decay-type behavior, but decreases in response to an increase in pH and possibly carbonate activity. As the pH decreases at later times, the lead activity increases due to both the decrease of carbonate activity, and the increased solubility of $Pb(OH)_2(s)$.

Two of the major ions, calcium and sulfate, also seem to be controlled to some extent by solid solubilities (graphs not shown). It appears that at early times $CaSO_4(s)$ controls the activity of the ions in solution, and at later times and higher pH values, $CaCO_3(s)$ may control activity. This may be the reason that calcium and sulfate do not exhibit the same mass transfer effects as observed with the other major ions.

The flux of zinc also appears also to be dependent on the solubility of certain solids, in this case $ZnSiO_3(s)$ and $Zn(OH)_2(s)$. As with lead activities, zinc does not display a simple decay as it is leached from the ash, but rather the activity increases at later times due to a decrease in pH and decrease in SiO_3^{-2} activity.

3.2 Modelling Approach

It is clear that a satisfactory description of leachate composition must involve interactions among several chemical components which produce a variety of chemical species ranging from discrete precipitates, as indicated above, to soluble complexes which comprise the total soluble concentration of a given chemical component. In addition, the advective and diffusive transport of components in the system must be considered in cases where chemical equilibrium reactions do not control solute concentrations. The general balance equation on each component, for one-dimensional non-dispersive transport through a homogeneous ash medium, is given by

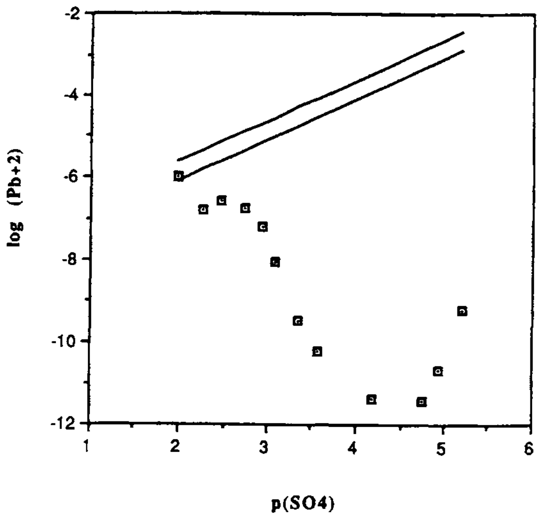

Figure 6a Log of lead activity vs. –log of sulfate activity. Solid lines represent the range of solubility constants reported in the literature for $PbSO_{4(s)}$.

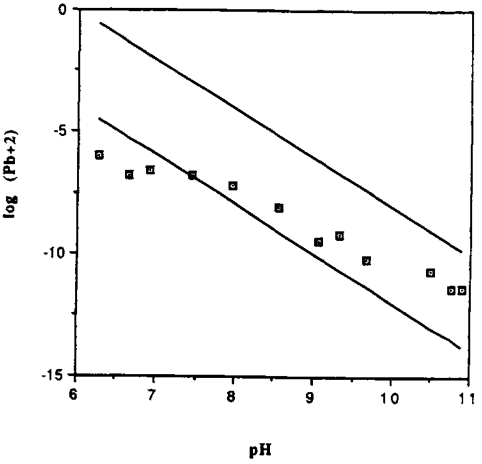

Figure 6b Log(Pb^{+2}) vs. pH; solid lines represent $Pb(OH)_{2(s)}$.

$$\frac{\partial u_i}{\partial t}+\sum_{j=1}^{N_p} A_{ij}\frac{\partial P_j}{\partial t}=-v\frac{\partial u_i}{\partial x}+\frac{\partial C_{si}}{\partial t}\left(\frac{1-\varepsilon}{\varepsilon}\right)+\frac{\partial \overline{C}_{pi}}{\partial t} \qquad i=1,N_c \tag{1}$$

where u_i is the total soluble (and therefore mobile) concentration of component i, P_j is the total concentration of precipitate j containing component i with a stoichiometry of A, C_{si} is the concentration of available (for release) component i on the ash solid surface, $\overline{C}_{pi}$ is the average concentration of component i in the interior matrix of the ash (available for diffusive flux), ε is the ash bed porosity, v is the interstitial velocity, and N_c and N_p are the number of components and precipitates, respectively. Additional balances for C_s and $\overline{C}_p$ on and within the ash particles are given by

$$\frac{\partial C_{si}}{\partial t}=ak_{ci}\left(C_{si}-u_i\right) \qquad i=1,\ N_c \tag{2}$$

and

$$\frac{\partial \overline{C}_{pi}}{\partial t}=\frac{\pi^2 D_{ei}}{R_p^2}\left(\overline{C}_{pi}-u_i\right) \qquad i=1,\ N_c \tag{3}$$

where a is the area to volume ratio of the ash particle, R_p is the average radius of the ash particles, k_c is the mass transfer coefficient for surface layer release, and D_e is the effective diffusion coefficient for transport from the interior of the ash particles.

The final equations for the model are the chemical mass action constraints with the functionality appropriate for the interactions of interest; for precipitates, for example, the general solubility product would be

$$K_j^{so}=\left[F\left(u_1,\ldots u_{N_c},A_{ij}\right)\right] \qquad i=1,N_c \quad j=1,N_p \tag{4}$$

It should perhaps be stressed at this point that the form of equation (4) will depend on the nature of the chemical interactions to be described. Thus, if sorptive controls on solubility are perceived to be of importance (as appears often to be the case, for example, for leachates from bottom ashes), then the proper functional form for (4) would be used (Theis and Wirth, 1977; Van der Hoek and Comans, 1996). Indeed for the strong base cations Na^+ and K^+, and also the anion Cl^-, chemical solubility controls do not seem to be important and their appearance in leachate is governed by mass transfer considerations alone.

The formulation of the problem is completed by stating the auxiliary conditions. Since the model will be applied to existing one-dimensional leachate data obtained in the laboratory, the most appropriate conditions on u and P are

$u_i(x,0) = 0 \quad i=1, N_c$ (5a)
$u_i(0,t) = 0 \quad i=1, N_c$ (5b)
$P_j(x,0) = 0 \quad j=1, N_p$ (5c)
$P_j(0,t) = 0 \quad j=1, N_p$ (5d)

Initial conditions for C_s and $\overline{C}_p$ are somewhat more problematic since it is difficult to obtain *a priori* information on the releasable concentrations of components. Batch leachate data may not accurately reflect the initial values since the measurements are generated under less than realistic conditions. The approach employed in this study was to use the integrated column leachate values (i.e. the total mass released during the column experiment) as a first approximation, that is

$$C_{si0} \geq \frac{1}{V_s}\int_{0}^{t_b} q \bullet u_{ti}\, dt \qquad i = 1, N_c \tag{6a}$$

and

$$\bar{C}_{pi0} \geq \frac{1}{V_s}\int_{t_b}^{t} q \bullet u_{ti}\, dt \qquad i = 1, N_c \tag{6b}$$

where u_{ti} is the experimental mini-column leaching curve for component i, q is the flow rate, and V_s is the volume of ash. The point b corresponds to the point of transition between surface mass transfer and diffusive release of material, and is estimated by inspection of the curve.

3.3 Model Results

As discussed above, it appears that various discrete precipitates control the concentration of several ionic species in the ash leachate, thus the solubility products given in Equation (4) are considered to be known and the parameters that need to be estimated are the mass transfer and effective diffusion coefficients for each component. In all, seven components were included in this analysis: Na, K, Ca, Mg, $S0_4$, Cl, and Pb. The procedure used was to discretize equations (1) through (4) and numerically approximate the solutions using a finite difference scheme. This solution algorithm is imbedded within a numerical parameter estimation procedure based upon the technique of Levenberg and Marquardt (Marquardt, 1963). Thus, equations (1) through (4) are solved with an initial set of values (in this case guessed values of ak_c and D_e), and the solution is compared with the experimental values using the sum of squared differences. The Levenberg-Marquardt method then governs the iteration to the point in parameter space corresponding to the minimum sum of squared differences. In the process, the Levenberg-Marquardt method generates sufficient information to produce the approximate joint ninety-five percent confidence intervals for both parameters.

The results of three of the model simulations are presented in Figures 7 through 9, in which the model output is compared with experimental data. Also shown are the estimates for ak_c and D_e along with error bounds (these error bounds represent the major axes of the joint 95% confidence region for the two-parameter set). Figure 7 illustrates the conservative behavior of potassium. This figure is also representative of the leaching curves for the other conservative components (magnesium, chloride, and sodium) in that no solid phase controls are predicted to influence the behavior of these solutes. As shown in Figures 2 and 3, however, the conservative solutes do appear in quite different concentrations, apparently in proportion to their abundance in the ash matrix.

Figure 8 shows the model predictions for the release of calcium from the ash matrix as well as the two estimated mass transfer coefficients. The figure demonstrates the prediction of calcium sulfate formation, which limits the release of the calcium (and sulfate) in the early stages of leaching (for the first 500 pore volumes or so). The mass transfer coefficients are also lower than seen in the conservative components indicating sorption may be important consideration in the release rates of some solutes.

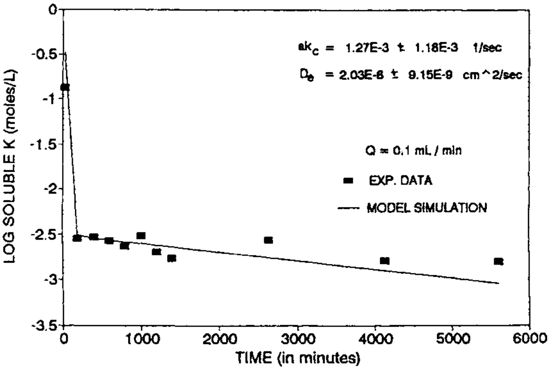

Figure 7 Log of potassium concentration vs. time. Line represents model simulation; parameter estimates with 95% confidence intervals shown on figure.

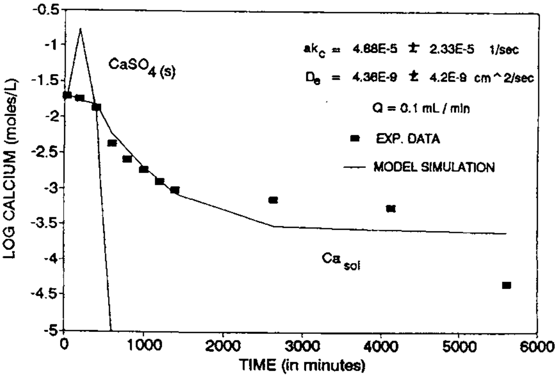

Figure 8 Log of calcium concentration vs. time. Line represents model simulation; parameter estimates with 95% confidence intervals shown on figure.

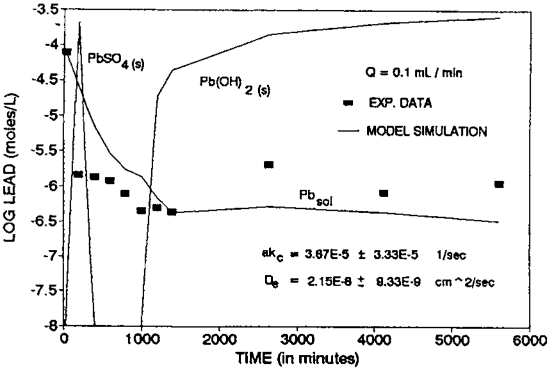

Figure 9 Log of lead concentration vs. time. Line represents model simulation; parameter estimates with 95% confidence intervals shown on figure.

Figure 9 compares predicted lead release rates with those observed in the dynamic leaching experiment. As demonstrated above with calcium, discrete precipitates are predicted to form. In this case, however, lead sulfate appears to limit lead solubility early in the leaching process, while lead hydroxide limits its concentration in solution at later times when there is an increase in pH and decay of sulfate concentrations. This transition was suggested by the thermodynamic speciation calculations discussed above, and are demonstrated to be predicted in this model formulation as well.

Figure 10 shows the estimated mass transfer coefficients in graphical form for the seven solutes studied along with the 95% confidence intervals for each estimate. The conservative components are estimated to have higher mass transfer and effective diffusion coefficients with one exception: the effective diffusion coefficient for lead. It is thought that, in general, lower estimates would be expected because of the retardation caused by sorption in the ash matrix and on the ash surface. It remains unclear precisely why the effective diffusion coefficient estimated for lead release is as high as it is. One hypothesis is that the controls on lead, for example by lead sulfate early in the leaching process, is a result of precipitate formation in the interstices of the packed bed. That is, lead and sulfate are leached from their respective "parent" minerals, and subsequently form lead sulfate. This phenomena was observed at the highest flow rate experiment (6.0 ml/min), in which a lead precipitate was formed after exiting the column reactor (i.e. the formation of the precipitate was not rapid enough and the solution exited the packed bed supersaturated). Thus, the formation of lead precipitates in the pores of the ash bed may result in a readily-available deposit, which in turn may result in the higher estimates for the effective diffusion coefficient of lead.

It is also quite likely, and is thought to be true in general, that the differences observed in the diffusion coefficients estimated are a result of different sorptive interactions during the leaching process.

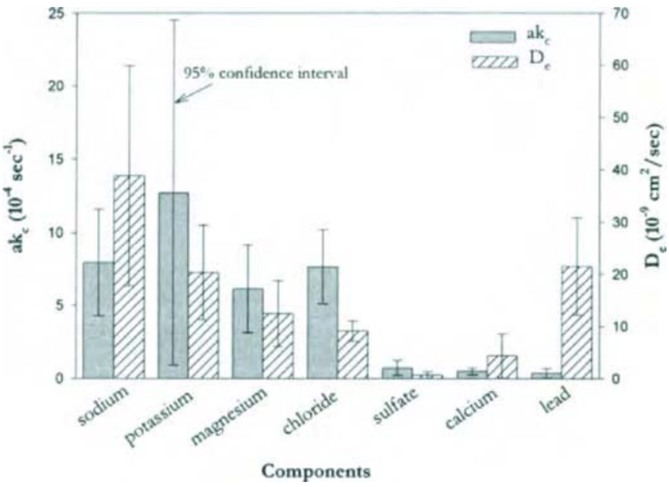

Figure 10 Estimates of mass transfer coefficients for all seven components investigated with 95% confidence intervals.

4. CONCLUSIONS

A set of dynamic leaching experiments were conducted on MSW fly ash, and a numerical model useful in the interpretation of the leaching curves was presented. Because of similarities to the leaching process in the environment, there is value in assessing the behavior of materials that are destined for either reuse or disposal in the manner presented here. The methods presented here demonstrate that the mechanisms controlling the concentration of solutes in leachate from ash materials are quantifiable. Further, the data and analysis presented here may be employed in a fate and transport model by providing a mechanistic approach to the prediction of the source strength.

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Waste Materials in Construction
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An initial investigation of the use of a rubber waste (EPDM) in asphalt concrete mixtures

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The need to improve the performance of asphalt concrete mixes for heavier traffic loads has led to several developments which include the use of polymers to improve asphalt cement (AC) properties resulting in Hot Mix Asphalt Concrete (HMAC) mixes with decreased temperature susceptibility, and increased resistance to rutting and load-associated. Polymer additives can also improve adhesion and cohesion and resistance to moisture-induced damage. A large quantity (300 Kilotons) of Ethylene Propylene Diene Monomer (EPDM) is produced by several industries in Louisiana each year. Of this, 1 to 5 percent represent residual waste and is being landfilled at a cost of \$50-\$70 per ton. The residual may be slightly out of specification or slightly contaminated, but the bulk properties of the material remain unchanged.

This paper reports a laboratory study of the potential for residual EPDM as a modifier of asphalt cement (AC). The study evaluated the engineering properties and moisture susceptibility behavior of HMAC containing EPDM modified asphalt cements.

The results indicate that residual EPDM has potential as an asphalt modifier.

1. INTRODUCTION

The need to improve the performance of asphalt concrete mixes for heavier traffic loads has led to several developments which include the use of additives, modification of the aggregate component and, an increase in the nominal aggregate size [Brown et. al., 1990; Lewandowski, 1994; Sherocman and Schutz 1992]. Addition of polymers has improved asphalt cement (AC) properties resulting in Hot Mix Asphalt Concrete (HMAC) mixes with decreased temperature susceptibility, and increased resistance to rutting and load-associated cracking [Brown, 1990; Button, 1992; Collins et. al., 1991; Khosla and Zahran 1989; Romine et. al., 1992; Terrel and Walter 1986]. Other benefits include increased thermal stability, greater resistance to damage related to age hardening, and non-load associated cracking [Khosla and Zahran, 1989; Lewandowski, 1994; Terrel and Walter, 1986]. Polymer additives can also improve adhesion and cohesion and resistance to moisture-induced damage [Terrel and Walter, 1986]. These improvements, coupled with the growing problem of disposal of waste rubber tires, have lead to the reprocessing of tire rubber for use in asphalt concrete mixtures.

A large quantity (300 Kilotons) of Ethylene Propylene Diene Monomer (EPDM) is produced by several industries in Louisiana each year. Of this, 1 to 5 percent represent residual waste and is being landfilled. The residual EPDM is an industrial waste that may be slightly out of specification or slightly contaminated, but the bulk properties of the material remain unchanged.

Residual EPDM represents a significant and costly management problem for producing industries and the state. Currently, such materials are disposed in permitted landfills at a cost of $50-$70 per ton. Valuable landfill space is being used for this potentially recyclable material while creating serious environmental problems such as fire hazards, mosquito breeding grounds, and contamination of ground water.

Utilization of residual EPDM in highway construction as an asphalt modifier, or in stabilized soil base courses, embankment fills, or concrete, could improve the performance of such systems and reduce disposal costs. This paper reports a laboratory study of the potential for residual EPDM as a modifier of asphalt cement (AC). The study evaluated the engineering properties and moisture susceptibility behavior of HMAC containing EPDM modified asphalt cements.

2. OBJECTIVE AND SCOPE

The primary objective of this research was to investigate the utilization of EPDM as a modifier of AC in HMAC mixes. A typical LADOTD dense graded mix was used. Four types of asphalt cements (AC-30, PAC-40 HG, EPDM modified AC-10 and EPDM modified AC-30) were investigated in the study of mix stiffness. A fifth asphalt cement (AC-10) was included in the moisture susceptibility study for which three types of commercial liquid anti-stripping (AS) additives were used. Indirect tensile strength, indirect tensile resilient modulus, and unconfined uniaxial creep tests were performed on the HMAC mixes to compare changes in mix stiffness. The modified Lottman test, boil test, (retained) resilient modulus test and (retained) Marshall stability test on Lottman conditioned samples, were used to study the moisture susceptibility of mixes.

3. MATERIALS

The HMAC mix selected was a dense graded mix of limestone and coarse and fine sands to meet the Louisiana Department of Transportation and Development (LADOTD) specification criteria for a Type 8 surface course [LA DOTD, 1992].

3.1. Aggregate

The aggregate composition was selected from an actual job mix formula and consisted of a combination of #78 SLS limestone, #11 SLS limestone, coarse natural river sand, and fine natural sand. The fine sand was hand-pulverized before sieving and only that portion that passed a No. 40 sieve was utilized in the washed sieve analysis and in the subsequent batch

TABLE 1 SUPERPAVE^{TM} BINDER SPECIFICATION TEST RESULTS

Test	Property	Asphalt Cement/Blend					Criteria
		AC-10	EPDM/ AC-10	AC-30	EPDM/ AC-30	PAC 40-HG	
		Original Binder					
Flash Point	n/a	n/a	n/a	n/a	n/a	n/a	230 ^{0}C min
Rotational Viscosity	135 ^{0}C	0.305	0.575	0.448	1.485	0.92	3 Pa. S. Max
Dynamic Shear Rheometer	G*/sin *	1.90 @ 58^{0}C	2.54 @ 70^{0}C	1.54 @ 64^{0}C	1.39 @ 76^{0}C	1.02 @ 70^{0}C	1.00 KPa min
		RTFO Aged Binder					
Mass Loss	n/a	< 1.00 %	< 1.00 %	< 1.00 %	< 1.00 %	< 1.00 %	1.00 % Max
Rotational Viscosity	135 ^{0}C	0.348	0.625	0.560	1.685	n/a	n/a
Dynamic Shear Rheometer	G*/sin *	3.06 @ 58^{0}C	2.30 @ 70^{0}C	3.35 @ 64^{0}C	3.03 @ 76^{0}C	2.47 @ 70^{0}C	2.20 KPa min
		PAV Aged Binder					
Rotational Viscosity	135 ^{0}C	0.535	0.715	0.873	1.940	n/a	n/a
Dynamic Shear Rheometer	G*sin * @ 25^{0}C	3212	1464	2836	3821	3403	5000 KPa Max
Bending Beam Rheometer	Stiffness @ -12^{0}C	243	111	198	185	99	300 MPa Max
Bending Beam Rheometer	m value@ -12^{0}C	0.48	0.39	0.33	0.35	0.452	0.30 min
PG GRADING		**58-22**	**70-22**	**64-22**	**76-22**	**70-22**	

proportioning of mixes. The mix had a maximum particle size of 19 mm, with 7.5 percent less than 0.075 mm.

3.2. Asphalt

The control asphalt cements were Lion AC-10, Lion AC-30 and Ergon PAC-40 HG. The two experimental asphalt cements were derived by modifying a Lion AC-10 and AC-30 each with three percent by weight of EPDM. This combination of asphalt cement source/grade and percent modification was based on previous studies of blends of EPDM and several sources and grades of asphalt cements. It was anticipated that the EPDM-modified AC-10 cement would provide HMAC mix properties comparable to those of conventional AC-30 mixes. An EPDM modified AC-30 cement was included in the experiment in anticipation that the modified mix would compare to a conventional PAC-40HG mix, which contains a styrene-butadiene-styrene modifier. Superpave binder specification tests were conducted on all the asphalt cements and the results are reported in Table 1.

3.3. EPDM

The EPDM material was supplied in "disks", approximately 1 to 3 mm in depth and 75 mm diameter, after polyvinyl alcohol pre-treatment. These disks were sliced into strips, approximately 2mm x 5mm x 5mm, then added to the heated asphalt cement. Blending of the EPDM particles into the asphalt cement required a high shear mixer operating at 175^0 C and 1500 rpm to achieve acceptable EPDM particle dispersion.

A potential problem with any polymer-modified AC is the miscibility of the polymer in the blend and the effects of this in the production and behavior of a HMAC mix. Utilizing a high shear mixing action produced acceptable EPDM particle dispersion in heated asphalt. Upon cooling and storage of the blend, EPDM particles segregated and rose to the top of the blend. However, simple re-mixing of the heated blend restored acceptable uniformity. Other than this potential storage problem, this study did not reveal any difficulties in the laboratory mixing, compaction, and testing of HMAC mixes containing EPDM modified AC's. A new blending method, in which EPDM particles are dissolved into the heated asphalt cement, is being currently developed.

3.4. Anti-stripping Additives

Three different commercial liquid anti-stripping (AS) additives (all amines) were used in the moisture susceptibility study. They are 1. Permatac-99® from Akzo Nobel Asphalt Applications, Inc. (AS# 1), 2.Pavebond T-Lite® from Morton International, Inc. (AS# 2), and 3. Adhere HP-Plus® from Arr-Maz Products, Inc. (AS# 3). A dosage rate of one half percent by weight of asphalt was used for all three AS additives according to LADOTD's specification [LADOTD, 1992].

4. EXPERIMENTAL PROGRAM

4.1. Mix Design

The HMAC mixes were manufactured using standard asphalt laboratory equipment and procedures, compaction of the mixes was by Marshall hammer. Marshall Mix design tests were conducted for the HMAC mixes over a range of asphalt cement contents (AC%). The National Asphalt Pavement Association (NAPA) method was then used to select the optimum AC% for three of the HMAC mixes. For the EPDM modified AC-30 HMAC mix, added later, the same AC% determined as optimum for the EPDM-modified AC-10 HMAC mix was used. Using the optimum AC% of each mix, test specimens were fabricated and arranged in groups of three, with an average air void content of 4.0% ± 0.2%, for conducting the engineering property tests.

4.2. Engineering Properties Testing

Specific gravity tests, density and air void analyses, and Marshall stability/flow (LADOTD TR 305M/305-96) tests were performed on all specimens. Indirect tensile strength (ASTM D 4867-92), indirect tensile resilient modulus (ASTM D 4123), and unconfined uniaxial static creep (Tex-231-F) tests were performed on selected specimens.

4.3. Moisture Susceptibility Testing

The modified Lottman test (AASHTO T283), the Louisiana ten minute boil test (LADOTD TR 322M/322-97), and the indirect tensile resilient modulus test and Marshall stability test on Lottman conditioned samples were used to study the moisture susceptibility of EPDM modified HMAC mixes. All the moisture susceptibility tests were conducted with and without the anti-stripping additives.

5. DISCUSSION OF RESULTS

A multivariate statistical evaluation of significance, ANOVA, was performed for each test property. The ANOVA analysis differentiates each group mean that is statistically different from other group means by use of categorical labels (A, B, AB, etc.). For example, a group mean that has a ranking "A" is significantly higher than the group mean that has a ranking "B". A designation of "AB" shows that the group mean can be placed into either statistical group. Group means with the same rankings are not statistically different.

In the discussion of results, the following convention is used to designate the five mixes:

A10- Conventional AC-10 HMAC mix
E10 - EPDM modified AC-10 HMAC mix
A30 - Conventional AC-30 HMAC mix
X30 - EPDM modified AC-30 HMAC mix
P40 - Commercial polymer modified (PAC-40HG) HMAC mix

The results of Marshall stability and flow test, indirect tensile resilient modulus test and modified Lottman test alone are discussed in this paper. A detailed discussion on other test results pertaining to this study can be found elsewhere [Metcalf and Waters, 1999; Gopalakrishnan et. al., 2000].

5.1. Marshall Stability and Flow

The mean Marshall stability and flow characteristics are shown in Table 2. Additionally, the statistical grouping designation is given for each mean value.

All four mixes met the LADOTD requirements for Marshall Stability and Flow for a Type 8 surface course [LA DOTD, 1992]. The E10 Stability value was not significantly different than that of the AC-30 mix, but was significantly lower than the P40 mix. The difference between mean Flow values of the four mixes was not significant. This indicates that the EPDM modification of a low-viscosity AC (i.e., AC-10) increased the stability of the mix to that of a typical AC-30 mix without significantly affecting the Flow characteristics.

TABLE 2 MARSHALL TEST RESULTS AT 60^{0}C

	Stability – Mpa 12.4 (min.)			Flow – mm 1.5 – 3.8			Air voids – percent	voids filled with asphalt - percent
Mixture ID	mean	std. dev.	group	mean	std. dev.	group	3.0 – 5.0	70 - 80
E10	15.2	1.14	B	3.1	0.38	A	3.9	71.8
A30	17.4	1.45	B	3.0	0.58	A	3.9	70.8
P40	23.3	0.59	A	3.5	0.61	A	4.1	70.0
X30	22.7	0.45	A	3.3	0.25	A	3.9	72.1

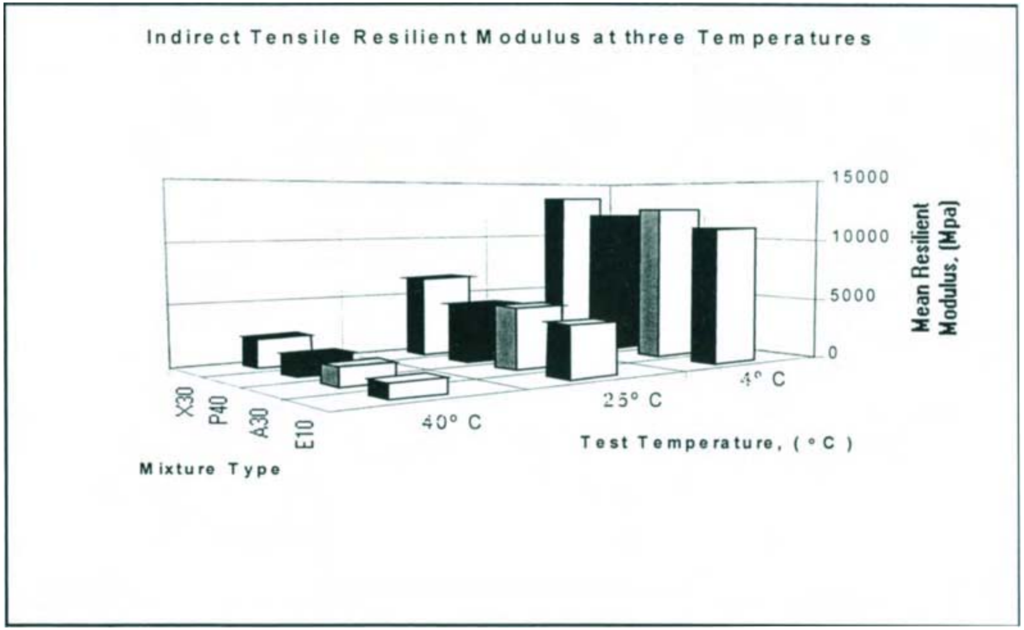

FIGURE 1 INDIRECT TENSILE RESILIENT MODULUS TEST RESULTS

TABLE 3 RESULTS OF MODIFIED LOTTMAN TEST (COMPARISON BY MIX TYPE)

Mix ID	Anti-stripping Additive															
	No Anti-strip				AS# 1				AS# 2				AS# 3			
	Ctrl. Str. (KPa)	Cond. Str. (KPa)	TSR (%)	Group	Ctrl. Str. (KPa)	Cond. Str. (KPa)	TSR (%)	Group	Ctrl. Str. (KPa)	Cond. Str. (KPa)	TSR (%)	Group	Ctrl. Str. (KPa)	Cond. Str. (KPa)	TSR (%)	Group
A10	744	434	**58**	**AB**	641	544	**85**	**A**	434	400	**92**	**A**	296	248	**85**	**AB**
E10	703	296	**42**	**B**	710	634	**89**	**A**	462	324	**70**	**B**	420	379	**90**	**AB**
A30	1337	772	**58**	**AB**	1075	958	**89**	**A**	765	517	**68**	**B**	510	413	**81**	**B**
X30	1474	620	**42**	**B**	1075	834	**78**	**A**	882	620	**70**	**B**	524	413	**79**	**B**
P40	1309	1006	**77**	**A**	1075	1000	**93**	**A**	792	565	**71**	**B**	531	496	**94**	**A**

Ctrl. Str. - Control Mean Indirect Tensile Strength, KPa
Cond. Str. - Moisture Conditioned Mean Indirect Tensile Strength, KPa
TSR - Tensile Strength Ratio, %

TABLE 4 RESULTS OF MODIFIED LOTTMAN TEST (COMPARISON BY ANTISTRIPPING ADDITIVE)

Anti-Stripping Additive	Mix ID																			
	A10				E10				A30				X30				P40			
	Ctrl. Str. (KPa)	Cond. Str. (KPa)	TSR (%)	Group	Ctrl. Str. (KPa)	Cond. Str. (KPa)	TSR (%)	Group	Ctrl. Str. (KPa)	Cond. Str. (KPa)	TSR (%)	Group	Ctrl. Str. (KPa)	Cond. Str. (KPa)	TSR (%)	Group	Ctrl. Str. (KPa)	Cond. Str. (KPa)	TSR (%)	Group
No Anti-strip **AB**		744	434	**58**	**B**	703	296	**42**	**C**	1337	772	**58**	**C**	1474	620	**42**	**B**	1309	1006	77
AS# 1	641	544	**85**	**A**	710	634	**89**	**A**	1075	958	**89**	**A**	1075	834	**78**	**A**	1075	1000	**93**	**A**
AS# 2	434	400	**92**	**A**	462	324	**70**	**B**	765	517	**68**	**BC**	882	620	**70**	**A**	792	565	**71**	**B**
AS# 3	296	248	**85**	**A**	420	379	**90**	**A**	510	413	**81**	**AB**	524	413	**79**	**A**	531	496	**94**	**A**

Ctrl. Str. - Control Mean Indirect Tensile Strength, KPa
Cond. Str. - Moisture Conditioned Mean Indirect Tensile Strength, KPa
TSR - Tensile Strength Ratio, %

The X30 mix displayed a significantly greater mean stability than that of the A30 mix, but was not significantly different than that of the P40 mix. The X30 flow value was not significantly different than either the A30 or the P40 mixes.

Comparing the two EPDM modified mixes, it was found that, as the base asphalt cement increases in viscosity grade (i.e., from an AC-10 base to an AC-30), the modification by EPDM caused a significant increase in stability (i.e., X30 stability > E10 stability). The flow values for the two modified mixes were not significantly different.

5.2. Indirect Tensile Diametrical Resilient Modulus (M_R)

Mean values for the M_R test at three test temperatures, 4^0 C, 25^0 C, and 40^0 C, are displayed in Figure 1. A higher M_R value is desirable at medium and high service temperatures where resistance to permanent deformation is required. It can be seen that a general M_R trend occurs for all mixes at the three test temperatures, with the M_R increasing from E10 to A30 to P40 to X30.

The E10 M_R is significantly lower than both the A30 and P40 control mixes at all three test temperatures. The X30 M_R is significantly greater than both the A30 and P40 control mixes at all three test temperatures.

5.3. Modified Lottman Test

Table 3 gives the response of five mix types for each anti-stripping additive in terms of Tensile Strength Ratio (TSR), and in Table 4, a comparison by anti-stripping additive is presented. The TSR value in the modified Lottman test is an indication of the potential for moisture damage. Higher TSR value indicates greater resistance of the mix to moisture damage. Based on his correlation studies, Lottman suggested a minimum value of 70 percent to pass the test [Lottman, 1982]. However, the LADOTD uses a minimum TSR value of 80 percent.

From Table 3, it could be seen that the P40 mix has the highest TSR value and highest statistical ranking whereas the E10 and E30 mixes show the lowest without any anti-stripping additive. The TSRs of A10 and A30 mixes are statistically similar. Also, all five mixes failed to meet the LADOTD's minimum TSR requirement of 80 percent when performed without any anti-stripping additive. Thus, all five mixes require an anti-stripping additive in order to meet the minimum LADOTD TSR requirement. Addition of the anti-stripping additive, AS#1, improved the TSRs of all the five mixes, though the E30 mix still fails to meet the minimum TSR requirement. When the test was performed with AS#2, all the mixes except A10 failed the test. Using the anti-stripping additive, AS#3, all the mixes, except E30, passed the test. In general, the P40 mix had a significantly higher TSR than the other mixes tested. Also, the addition of AS#1and AS#3 have significantly improved the stripping resistance of all the five mixes as measured by the TSR.

From Table 4, it is clearly seen that all the three anti-stripping additives: AS#1, 2 and 3 have the same effect on the A10 mix and make it meet the minimum LADOTD TSR requirement. In case of the E10 mix, AS#1 and 3 are equally effective. A similar trend is found in the A30 mix. Both additives, AS#1 and 3, have the same effect on the A30 mix and make it pass the test. All the three additives have the same statistical effect on the E30 mix and it fails the test. In the case of P40 mix, AS#1 and 3 have the same effect and the mix passes the test with these two additives.

It is clearly seen from these results that AS#1 is the only anti-stripping additive that has significantly improved the TSR of all the five mixes without causing a significant reduction in the control tensile strength of all the five mixes. Even though AS#3 is equally effective, the

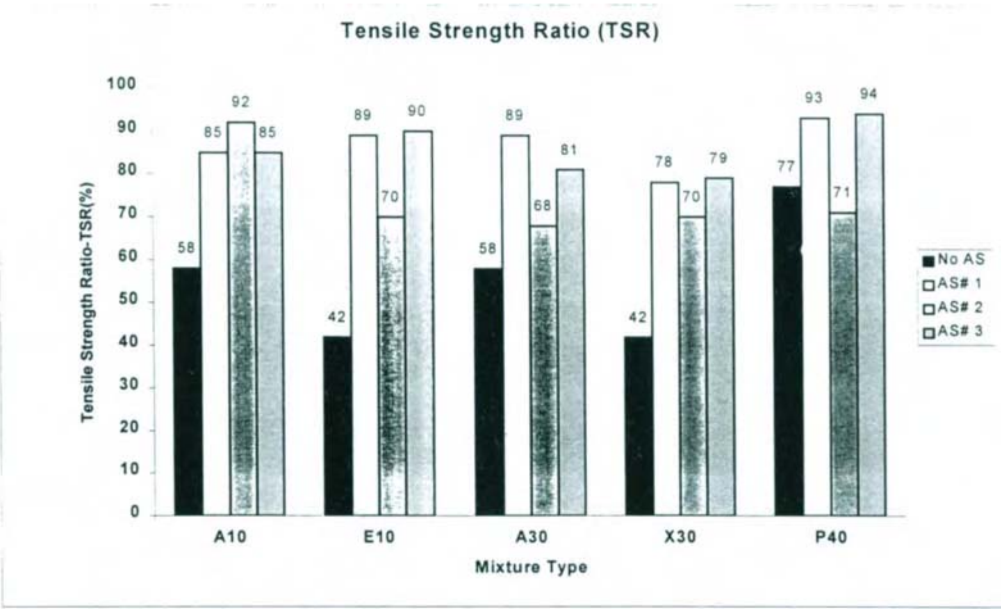

FIGURE 2 MODIFIED LOTTMAN TEST RESULTS

control tensile strengths have reduced significantly on using this anti-stripping additive. Figure 2 shows the results of modified Lottman test.

6. CONCLUSIONS

The study shows that a typical job mix formula of HMAC with EPDM modified AC can be mixed and fabricated in the laboratory using standard equipment and mix design procedures. The results of the study can be summarized as:

1. EPDM modified AC-10 HMAC mixes (i.e., E10) compared favorably to conventional AC-30 HMAC mixes (i.e., A30) in terms of Marshall stability and flow, indirect tensile strength, and creep properties.

2. Compared to typical PAC-40HG HMAC mixes (i.e., P40), the E10 mixes performed favorably in terms of Marshall flow, indirect tensile strain at failure, creep stiffness, permanent strain, and creep slope.

3. EPDM modified AC-30 HMAC mixes (i.e., X30) performed better than unmodified AC-30 HMAC mixes (i.e., A30) in terms of Marshall stability, indirect tensile strength at 25^0 C and 40^0 C, and resilient modulus at 4^0 C, 25^0 C, and 40^0 C.

4. The X30 mixes performed as well or better than the P40 mixes in terms of Marshall stability, Marshall flow, indirect tensile strength at 25^0 C and 40^0 C, indirect tensile resilient modulus at 4^0 C, 25^0 C, and 40^0 C, and creep stiffness.

5. The results of the moisture susceptibility study shows that the EPDM modified HMAC mixes are prone to stripping and hence require an anti-stripping additive. The use of AS# 1 as an anti-stripping additive was very effective in both conventional and EPDM modified HMAC mixes.

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Waste Materials in Construction
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Immobilisation of PAH in waste materials

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This paper gives an overview of the results of a research project into the possibilities of immobilising polycyclic aromatic hydrocarbons (PAH), that are present in waste materials. The results show that with hydraulic binders the waste materials can be solidified. The PAH do still leach to a relatively high extent. However, this PAH leaching can be decreased by more than a factor 10 by means of the addition of a specific additive. The immobilisation product fulfils technological requirements for the use as a road base construction material, such as compressive strength.

1. INTRODUCTION

There are several waste materials that contain, beside heavy metals, relatively high concentrations Polycyclic Aromatic Hydrocarbons (PAH) and other hydrocarbons, such as mineral oil. For instance sieve sand (the fine fraction of demolition waste) and washing sludge of this sieve sand contain PAH in amounts, varying from 10 to 200 mg/kg. These PAH mainly originate from roofing material and soot from chimneys. Also dredging sludge often contains relatively high amounts of PAH.

The Dutch Building Materials Decree (BMD) sets limits for the content of PAH in building materials (50 - 75 mg/kg). Because of these regulations, the direct use of these types of waste is prohibited, and large amounts of these materials have to be disposed of. However, for protection of the environment not the total amount of a component in the material is of concern, but the amount that can leach out. So, it would be reasonable to base the regulations on leaching limits. Unfortunately, the condition of a reliable leaching test for organic components was not fulfilled when the Building Materials Decree was prepared. Nevertheless, significant progress has recently been achieved in this respect with a modification of the Dutch diffusion test (tank leaching test) [1]. This enables the quantification of the effectiveness of immobilisation (stabilisation / solidification) of PAH containing waste materials.

In the investigation, described below, a combination of sieve sand and washing sludge as well as a dredging sludge were immobilised in such a way that the product, physically, could be used as a road base construction material. The environmental impact of the use of such a material was assessed on the basis of the results of leaching tests.

So, the aim of the study was to develop a recipe for the effective immobilisation of the above mentioned waste materials with a combination of a cement-based binder and an additive. Physically the product needs to fulfil the criteria, set for sand-cement stabilisation layers in road construction. Environmentally the aim was to substantially decrease the leaching of PAH, to an acceptable level [2].

2. IMMOBILISATION OF PAH

For the chemical immobilisation of PAH the use of hydraulic binders (e.g. cements) is not sufficient. The PAH-molecules cannot be built into the cement matrix. Nevertheless, physical encapsulation in the matrix may occur, to some extent. However, a better way of immobilising PAH is to apply some kind of additive, that is able to form a physico-chemical bond with the PAH. Subsequently, the additive is then built into the cement matrix. In this way the PAH is indirectly bound. In the research project 2 types of additives have been applied. Also different hydraulic binders were used, primarily chosen for the ability to develop strength, despite the presence of impurities, like organic matter, chloride salts and sulphates [3].

3. EXPERIMENTAL METHODS

The test specimens were prepared by mixing the ingredients thoroughly, adding the hydraulic binder, additive and water, mixing again, moulding the mixture and compacting. The specimens were put in a climate cell for 28 days to harden. Afterwards they were tested.

The physical testing consisted of measuring the compressive strength as well as the density in triplicate.

The leaching of PAH from the prepared products was studied with a modification of the Dutch diffusion test (NEN-7345) [4]. The diffusion test (tank leaching test) is carried out by placing a sample in a tank, which is filled with acidified leachant. The leachant is replaced according to a specified time schedule. In some cases the replacement scheme was modified, in order to shorten the test: the standard test lasts for 64 days, whereas some tests were carried out in a period of 16 or 25-days. The modifications consisted of some pre-cautions, that were taken to prevent the degradation and/or the absorption of leaching PAH. The pre-cautions were:

- The leaching vessel was made of glass and covered, to avoid evaporation of the more volatile PAH.
- The leaching vessel was packed in aluminium foil, to prevent degradation of PAH by ultra-violet radiation of sunlight.
- The eluates were filtered in Teflon filter devices, by means of pressure filtration, to avoid absorption of PAH in the device.
- The eluates were put in brown flasks in between the time of sampling and the time of analysis, again to avoid degradation of PAH.

4. CHARACTERISATION OF WASTE MATERIALS

In this research project experiments were carried out with a combination of sieve sand and sludge from the washing of sorting sieve sand. Originally it was the intention to do the experiments with washing sludge only, but to get a reasonable strength development, a more coarse fraction had to be added. For that reason sieve sand was added.

Besides, also dredging sludge has been subjected to immobilisation experiments. Also in this case, experiments pointed out that a coarser fraction had to be added, in order to get enough strength development. In this case clean sand was added.

All waste materials have been subjected to chemical analyses and availability leaching tests. None of them fulfilled all criteria of the Building Materials Decree with respect to total contents of PAH and/or mineral oil and/or with respect to sulphate leaching.

The results of the chemical analyses and the leaching tests on sieve sand and the sludges are given in table 1.

It should be noticed that especially the dredging sludge is a very fine material, with a relatively large amount of easily leachable chloride salts.

Table 1

Results of the characterisation of the waste materials to be immobilised

		sieve sand	washing sludge	dredging sludge
particle size	d_{50} [μm]	800	60	10 – 20
	d_{90} [μm]	8,000	350	60
moisture content [wt%]		16.3	46.6	> 80
loss on ignition [wt%]		3.9	13.7	14.5
total content of 10 PAH (mg/kg)		92	119	30
total content of mineral oil (mg/kg)		-	-	1300
Availability for leaching of sulphate [mg/kg]		33,000	68,000	4,000
Availability for leaching of chloride [mg/kg]		-	-	23,000

5. IMMOBILISATION OF PAH IN SIEVE SAND AND WASHING SLUDGE

In order to demonstrate the possibilities of immobilisation of PAH, a research has been conducted to develop building materials from sieve sand and washing sludge thereof, both contaminated with PAH beyond the regulatory limits concerning total PAH contents.

Exploratory experiments have been performed, in which special additives were added to the wastes, to bind organic compounds, especially PAH.

5.1 Preliminary experiments

In a series of preliminary experiments two different types of additives were assessed, concerning their ability to bind PAH. In this stage no hydraulic binders were added, just to find out whether the additives were able to bind the PAH in a physico-chemical way, without any entrapment in a solidified matrix. The two additives (A1 and A2) were added to a slurry of sieve sand, washing sludge and water, in a ratio of 1:1:1. This mixture was agitated on a roller table for 6 hours, to get a thorough contact between the waste materials and the additives. After the six hours water was added up to a liquid to solid (L/S) ratio of 2 l/kg, and the mixture was agitated for another six hours, as is prescribed in draft prEN 12457, part 1 [5]. Afterwards the eluate was filtered over a 0.45 μm membrane filter, and analysed on 10 PAH. The additives were added in amounts of 0, 1.5 and 3 weight % (dry matter). In one case some lime was added, to simulate a high pH, as will be the case after solidification with a hydraulic binder. The results of these preliminary experiments are given in table 2. The mixture of waste materials contained 102 mg/kg of PAH.

Table 2
Results of preliminary experiments with additives to bind PAH

exp. no.	additive type	additive content [wt%]	pH of eluate	leaching of PAH [μm/kg dm]	relative leaching of PAH [%]
1	-	-	7.4	9.6	0.0094
2	A1	1.5	7.4	1.9	0.0018
3	A1	3.0	7.3	2.5	0.0025
4	A1 + lime	1.5 + 3.0	12.4	4.0	0.0039
5	A2	1.5	7.8	0.7	0.0007
6	A2	3.0	7.9	0.6	0.0006

In general it can be concluded from table 2 that the PAH do not easily leach, due to their low soluability. Besides, it is clear, that the additives have an influence on the leaching of PAH; addition of A1 decreases the PAH leaching with a factor 4 to 5, addition of A2 with a factor 12. So, additive 2 appears to bind the PAH better than additive 1; A2 was selected for further experiments. The results also make clear that the addition of 1.5% of additive is at least sufficient. The experiments with lime addition shows that the PAH are at high pH more mobile than at neutral pH.

5.2 Recipe development

After the preliminary experiments, real immobilisation experiments were carried out, with addition of hydraulic binders and additive. In a first series of experiments (1 – 3) a blend of two hydraulic binders was used, in a ratio of 3 : 1. A relatively high amount of binder was used (21 wt%), because of the fineness of especially the washing sludge. Because of the less thorough mixing of binder, additive and waste materials, the same quantities of additive were used as in the preliminary experiments. Test pieces were prepared with 21% binder and hardened for 28 days. Then compressive strengths were measured and one of the pieces of each type was tested for 16 days in the modified diffusion test. From these test results PAH emissions (= leaching per m^2 product surface area) after 64 days were calculated by means of extrapolation. Also, PAH immissions (leached quantities, entering the soil, per m^2 soil surface area) in 100 years were calculated, according to the methods prescribed for inorganic components from a category 1 construction material by the Dutch Building Materials Decree.
After this first series of experiments two additional types of specimens were prepared (experiments 4 and 5). Now a little less hydraulic binder was used, as well as less additive (0.7 wt%), based on the results of experiments 2 and 3. In experiment 5 another binder was used. Also these specimens were tested after 28 days. Now the modified diffusion test was extended to 64 days (as is prescribed in the standard). Again immissions were calculated on the basis of the emissions measured in the tests.
The results of all experiments (1 – 5) are shown in table 3. Experiment 2 (a and b) shows that the way and intensity of mixing and compacting is important for the strength development. Test pieces were made with the same constituents. Now, the compacting was less well, as can be derived from the lower density, caused by a poor workability of the material. This leads to a

lower compressive strength. Nevertheless, the leaching of PAH from sample 2b is only a little lower than that from sample 3, indicating that the leaching of PAH does not primarily depend on the physical retention, caused by the porosity (= tortuosity) of the matrix, but on the chemical retention, caused by (physico-)chemical bonds to the additives. This is also pointed out by the results of experiments 4 and 5. The specimens have lower densities and are less strong, but nevertheless the leaching does not increase, but even decreases.

Table 3: Results of recipe development for PAH immobilisation of sieve sand and washing sludge

exp. no.	binder type	binder content [wt%]	additive type	additive content [wt%]	density [kg/m^3]*	compressive strength [MPa]*	PAH leaching [mg/m^2] emission in 64 days	PAH leaching [mg/m^2] immission in 100 years**
1	B1 + B2	21	-	-	1740	5.2	14.0	150
2a	B1 + B2	21	A2	1.5	1730	4.9	-	-
2b	B1 + B2	21	A2	1.5	1690	1.8	0.23	2.5
3	B1 + B2	21	A2	3.0	1710	5.1	0.20	2.1
4	B1 + B2	16	A2	0.7	1620	2.6	0.15	1.6
5	B3	20	A2	0.7	1610	1.1	0.12	1.2

* measured 28 days after manufacture

** calculated according to methods prescribed in Building Materials Decree; upper allowable limit for PAH is not given in the BMD, but can be derived in the same way as for inorganics (= 15 mg/m^2)

The results in table 3 clearly show that the presence of a certain amount of additive is required for a good immobilisation of the PAH. The leaching of PAH from mixture 1 (without additive) is extremely high, compared to that from the other mixtures (with additive). On the other hand do the results show that more additive does not lead to a better immobilisation of PAH; even 0.7 wt% of additive is enough to decrease the leaching of PAH substantially.

The results of experiment 5 indicate that not only the additive, but also the type of hydraulic binder is relevant for the degree of immobilisation. Despite the low compressive strength, the leaching of PAH from mixture 5 is the lowest. On the other hand it is clear that binder B3 is less effective in strength development than the blend of binders B1 and B2. Even the 20 wt% of binder B3 is not enough to fulfil the requirements (3 - 5 MPa after 28 days of hardening) for the application as a road construction material. There is no indication that the strength development is influenced by the presence of more or less additive (nor in a negative sense, nor in a positive sense).

As was mentioned in the introduction, the Dutch Building Materials Decree for organic components sets limit values to the total content and not to the environmentally more relevant leaching of these components. To be able to assess the degree of immobilisation, emissions from the immobilisation product were calculated (in terms of mg per m^2 of product surface area), as well as immissions to the soil, caused by such emissions (in terms of mg per m^2 soil surface area). The immissions were calculated in the same way as is prescribed for inorganic components in the Building Materials Decree. The immissions were calculated for so called ‘category 1’ construction materials (that may be used in all situations, without any provisions to prevent contact with rain or ground water).

Also an upper allowable immission limit value was derived for PAH, by analogy with the derivation for inorganic components, based on the principle of 'marginal burdening' of the soil. Thus, an upper allowable immission of 15 mg/m^2 was calculated. Compared with this limit value, the immobilisation product without additive (no.1) would not fulfil the criteria, and would not be allowed to be used as a category 1 construction material. All products with additive show immissions that are far below this limit value. This, and the fact that even an additive addition of 0.7 wt% did not show a higher leaching than an addition of 3.0 wt%, lead to the recommendation to further decrease the amount of additive in future work. A combination of 18 wt% of the blend of binders B1 and B2 or approximately 22 wt% of binder B3 and approximately 0.4 wt% of additive A2 seems to be sufficient to immobilise a mixture of sieve sand and washing sludge in such a way that it fulfils technological and environmental requirements.

From the leaching results the conclusion can be drawn that, though the waste materials do contain high levels of PAH (according to the Building Materials Decree), they can be immobilised in such a way that the leaching of PAH does not cause any harm to the environment.

6. IMMOBILISATION OF PAH IN DREDGING SLUDGE

In The Netherlands many harbours and water ways have contaminated sediments. The most contaminated dredging sludges from those sites are being disposed of in large lagoons. However, the societal resistance against the construction of such disposal sites, is increasing. This offers good prospects to the development of processing technology, leading to the useful application of the product. One of these opportunities is the use of stabilised dredging sludge as a road base construction material. Obviously, this requires a sufficient immobilisation of the pollutants that are present in the dredging sludge.

Because of the fact that many dredging sludges are contaminated with PAH, in this research project also dredging sludge was used as a case in the development of a recipe for the immobilisation of PAH. Additional problems with dredging sludge are the fineness of the material, the relatively high amount of organic matter and, in the sludge from sea harbours, the salt content.

6.1 Selection of an additive for binding the PAH

The development of a recipe for the immobilisation of PAH in dredging sludge was executed in two steps. In the first step an effective additive was selected in experiments without hydraulic binders. This step was followed by a second step, in which hydraulic binders were added, to get a solidified material that should meet technical as well as environmental requirements.

For dredging sludge, the same two additives A1 and A2 were tested, as was done in the case of the mixture of sieve sand and washing sludge (see 5.1). In the case of dredging sludge higher amounts of additive were used (2.5 and 5 wt%), because of the existence of large amounts of organic matter and relatively high concentrations of mineral oil. The dredging sludge and the additive were thoroughly mixed and then leached at L/S = 2 l/kg. The results of these experiments are given in table 4. The total content of PAH in the dredging sludge was 30 mg/kg dry matter.

Table 4: Results of experiments to select an additive for binding PAH in dredging sludge

exp. no.	additive type	additive content [wt%]	pH of eluate	leaching of PAH [μm/kg dm]	relative leaching of PAH [%]
1	-	-	8.5	10.0	0.25
2	A1	2.5	7.8	1.9	0.051
3	A1	5.0	7.8	1.4	0.041
4	A1 + lime	2.5 + 5.0	12.4	2.8	0.078
5	A2	2.5	8.3	1.1	0.033
6	A2	5.0	8.4	1.2	0.035

The conclusions are more or less the same as with the mixture of sieve sand and washing sludge (see 5.1). The differences between the experiment without additive and the others is not very large, but still a factor 5 to 8. Also the difference between additive A1 and A2 are less, but still it is clear that A2 performs better. Again the pH-effect is shown and doubling the dose of additive does not increase the binding capacity.

Additive A2 was chosen for further investigations, and it was decided that in the experiments with the hydraulic binders the quantity of additive would be halved.

6.2 Different behaviour of the individual PAH

To get more insight in the capability of the different additives to bind the PAH, the results of the above mentioned experiments were analysed for all individual PAH that are entered in the Dutch Building Materials Decree. These are the ten PAH of the Dutch Ministry of Environment (VROM): naphthalene, phenanthrene, anthracene, fluoranthene, benzo[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene and indeno[123cd]-pyrene.

Table 5: Results of PAH-binding experiments, for individual PAH

component	total content in dry sludge [mg/kg]	solubility in water of 11 °C [μg/l]	leached from sludge with / without additive [μg/kg]					
			without additive	2.5% A1	5.0% A1	2.5% A1 + 5% lime	2.5% A2	5.0% A2
naphthalene	4.2	16,000	8.19	0.74	0.46	1.15	0.14	0.25
phenanthrene	1.8	630	0.46	0.22	0.17	0.37	0.16	0.17
anthracene	0.8	37	0.05	0.04	0.04	0.09	0.03	0.03
fluoranthene	8.9	130	1.17	0.74	0.62	1.01	0.60	0.62
benzo[a]anthracene	2.4	7	0.01	<0.01	0.01	<0.01	0.03	<0.01
chrysene	2.2	1	0.03	<0.02	<0.02	<0.02	0.04	<0.02
benzo[k]fluoranthene	0.9	0.3	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01
benzo[a]pyrene	6.5	0.2	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
benzo[ghi]perylene	1.6	0.2	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
indeno[123cd]pyrene	1.4	0.1	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
sum 10 PAH	30.7		10.0	1.88	1.44	2.76	1.12	1.22

In table 5 the total content of the individual PAH is given in the second column, in terms of mg/kg dry matter. Also the solubility of the individual PAH in water is given, as an indication of what potentially could leach. Besides, the quantities that were leached in the tests are given, expressed in µg/kg dry matter. The following conclusions can be drawn from these experimental results:

- All ten PAH are present in the dredging sludge, especially fluoranthene, benzo[a]pyrene and naphthalene.
- The more heavy PAH do not leach, nor in the situation with additive, neither without; only the four lightest PAH do leach to some extent. This is in accordance with the degree of solubility of the PAH, though the potential is still much higher than the actual leaching.
- In the situation without additive addition especially naphthalene contributes to the leaching of PAH (82% of the total quantity); also this is in agreement with the solubility figures.
- It is also naphthalene that is preferentially bound by the additives, especially by additive A2. On the other hand fluoranthene is only bound to a small extent. It seems that the lighter the PAH, the better they are bound by the additives.

6.3 Solidification experiments

After the selection of the best additive to bind PAH in dredging sludge, solidification experiments were carried out to process the immobilised material into an applicable construction material. Because the aim was to produce a road base material, the material had to fulfil requirement concerning compressive strength and concerning total content and/or leaching of organic and inorganic components (Building Materials Decree).

In a first series of experiments trials were made to solidify the dredging sludge with a hydraulic binder and additive. As hydraulic binder B1 was chosen, whereas A2 was selected as additive (see 6.1). Because of the higher content of very fine particles and of organic matter, a higher amount of binder (30 wt%) was added than in the previous experiments with sieve sand and washing sludge. As is shown in table 6, the compressive strength was still too low. For that reason a new series of test pieces were prepared, but now with a mixture of sludge and sand (for a better particle size distribution). Now the specimens developed (more than) enough compressive strength.

After 28 days the compressive strengths were measured and one of the pieces of each type was tested for 25 days in the modified diffusion test. Again from these test results PAH emissions after 64 days were calculated by means of extrapolation. From this, PAH immissions in 100 years were calculated, according to the methods, described in the Building Materials Decree for category 1 construction materials. All results are summarised in table 6.

The results of table 6 clearly show that 30 wt% of hydraulic binder B1 is not enough to solidify the dredging sludge. It might be possible to get better results with even higher amounts of binder, but that would become too costly. Therefore another option was chosen, namely to mix the sludge with sand. Many dredging sludges do already contain a certain amount of sand, but the investigated sludge didn't. In practice also (slightly) contaminated soil might be used to get a better (= coarser) particle size distribution. The addition of sand makes the material almost too strong; the compressive strength is 8 – 9 MPa, whereas the requirements are 3 – 5 MPa. So, in optimising the composition of the material, on the one hand the choice might be made for a lower binder content (approximately 25%) or, on the other hand, the addition of sand to the dredging sludge might be decreased.

Table 6: Results of the solidification experiments with dredging sludge

exp. no.	sludge / sand ratio [kg/kg]	binder content [wt%]	additive type	additive content [wt%]	density [kg/m³]*	compressive strength [MPa]*	PAH leaching [mg/m²] emission in 64 days	PAH leaching [mg/m²] immission in 100 years**
1	1 : 0	30	-	-	1470	0.4	-	-
2	1 : 0	30	A2	1.2	1470	0.2	-	-
3	1 : 0	30	A2	2.4	1430	0.2	-	-
4	1 : 1	30	-	-	1880	8.0	1.30	14.0
5	1 : 1	30	A2	1.4	1890	8.1	0.19	2.0
6	1 : 1	30	A2	2.6	1880	9.3	0.15	1.6

* measured 28 days after manufacture

** calculated according to methods prescribed in Building Materials Decree; upper allowable limit for PAH is not given in the BMD, but can be derived in the same way as for inorganics (= 15 mg/m²)

As is shown in figure 1, the addition of 1.4 wt% of additive decreases the leaching of PAH with a factor 7. Doubling of the additive content seems to further decrease the leaching of PAH, but not significantly. If the leaching results (immissions to the soil in 100 years) are compared with the limit value, derived in accordance with the "marginal burdening" principle of de Building Materials Decree (15 mg/m²), it appears that the solidified material without additive is on the borderline. The fact that the total PAH content in the dredging sludge was not too high, in combination with the good solidification (high density and high compressive strength), makes a physical encapsulation almost sufficient. Nevertheless, the addition of some additive brings the PAH immission far below the limit value.

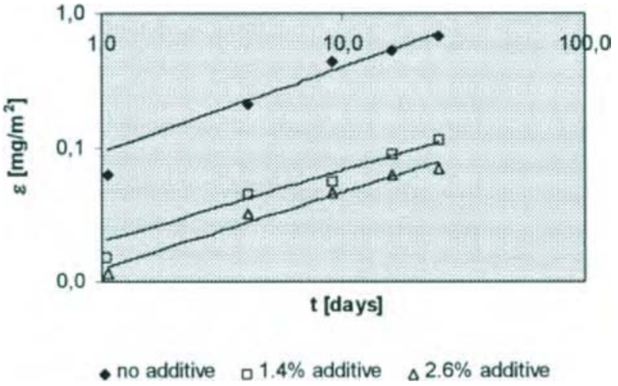

Figure 1: PAH emissions from immobilised dredging sludge

When the leaching of the individual PAH is observed, the analytical results indicate that the less toxic PAH components naphthalene and phenanthrene dominate the emission (together ± 90%). Fluoranthene is not leached substantially, even though in the preliminary experiments fluoranthene appeared not to be bound substantially by the additive (see 6.2). Obviously, not only the chemical bond, but primarily the physical resistance of the matrix retaines the fluoranthene molecules from leaching.

Figure 1 also points out that the PAH leaching from the solidified dredging sludge samples is controlled by the mechanism of diffusion. The lines are straight and the slope is approximately 0.5, according to Fick's law.

7. CONCLUSIONS and OUTLOOK

It appears possible to immobilise a mixture of sieve sand and washing sludge as well as a mixture of dredging sludge and sand in such a way that the leaching of Polycyclic Aromatic Hydrocarbons (PAH) is minimised. Moreover, the immobilisation product fulfils the criteria for an application as road construction material.

Additive A2 is capable to physico-chemically bind the PAH in such a way, that the leaching of PAH is largely reduced; by a factor of 7 to 10. Especially the 'lighter' PAH (naphthalene and phenanthrene) are bound by the additive. The heaviest, and most toxic PAH do not leach at all. The components in between (especially fluoranthene) are either bound by the additive, or entrapped in the physical matrix; they do leach only to a very little extent.

Based on the philosophy of the Building Materials Decree, an immission limit value was derived for PAH. The aim of the Decree is to protect the soil and groundwater against contamination, caused by leaching from (secondary) construction materials. The specimens, prepared with a hydraulic binder and an additive, can easily fulfil this limit value.

In the near future, demonstration projects will be organised in co-operation with local authorities and contractors, with a fine sieve sand (contaminated with sulphate and PAH), and with a sandy dredging sludge. During at least one year the actual leaching from these road parts, on a base of immobilised waste materials, will be monitored. The aim of the demonstration projects is to verify lab experiments on a pilot scale, to prove that immobilisation is environmentally and economically feasible, and that the product is a suitable road construction material. Besides, the demonstration project can be used to provide reference cases upon which present regulations can be modified.

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The Building Materials Decree: an example of a Dutch regulation based on the potential impact of materials on the environment

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Some 20 years ago Dutch society became very aware of the problem of the increasing production of waste materials and of the need to find solutions. Technical solutions had to be developed and introduced into society. Due to the discovery of many soil pollution problems and other environmental calamities, people asked for clear criteria on which proper and safe solutions could be based. Therefore a large number of environmental aspects had to be taken into account in the developing field of environmental policy.

The Dutch building materials decree (BMD) is one of the steps on the road towards a sustainable society. The decree is based on the soil protection act and the surface water protection act. The decree gives quality criteria for the application and re-use of stony materials and earth used as building materials. No difference is made between primary materials, secondary materials and waste materials. The decree is applicable in case these materials are used in constructions where they are in contact with rain, surface water and ground water (e.g. in embankments, road building, outside walls of buildings, foundations and roofs.) For implementation of the decree in the construction industry it was necessary to develop standards, methods for testing and certification schemes. In order to guarantee independent testing and judgement, laboratories had to meet quality standards put forward in an accreditation scheme.

Although this legislation does not cover all environmental aspects, it has proved to be an important element in judging the environmental quality of construction materials in a direct or indirect way, and a contribution to the management of waste materials. The question of clear and fair criteria was easily put forward. Answering this question, however, turned out to be a complex task in which a great number of aspects had to be considered and a great many tools had to be developed, checked and thoroughly discussed. In some cases practical choices had to be made in order to prevent an unclear situation continuing too long. After an introduction period of three years, the decree came into full operation on 1 July 1999.

1. INTRODUCTION

In the period from 1960 to 1980 the production of waste materials and secondary materials increased dramatically. A large part was dumped at waste disposal sites without adequate soil protection measures. Another part was used without treatment in embankments or other construction works, in many cases causing soil and surface water pollution. A small part was treated and reused in a more or less environmentally controlled way.

The introduction of the waste management act and the hazardous waste management act around 1976 offered instruments for regulating waste streams. Changing the way of dumping waste, without soil protection facilities, into well controlled ways of chain management or re-use proved not to be easy. Therefore additional legislation needed to be developed.

Many technical and policy programs were put into action to develop new products and new ways of usage, or for finding better ways of dumping if no other solutions remained. In the field of earth and stony materials, nowadays 15-20 million tons per year of secondary materials and waste materials are being re-used [9]. This is about 90% of the waste stream concerned. Not included is the amount of polluted soil and dredging sludge, the management of which is still under development. The results of the re-use of stony materials could only have been reached by carrying out a lot of work including research, standardisation and environmental standard setting in a controlled program, with synchronisation of the various activities. In the process of setting up the framework for this program many parties, including the construction industry, put forward the wish to judge materials not only on the basis of the total chemical composition of components in construction materials but also, or only, on the release (leaching) of components. It was argued that the release was of more importance regarding soil pollution than the total chemical composition. This resulted in the development of standard leaching tests being included in the program. After 10 years of research, a number of release tests have been developed; data obtained with these tests on many materials has been collected. Based on this data a certain insight into the mechanism of release in laboratories and in practice occurred. Development of models was needed for this analysis.

During the execution period of the program some important developments took place in the field of soil protection, e.g. the introduction of the Soil Protection Act in 1987; the development of target values for soil quality and the development of intervention values for soil pollution. These developments made an important input to the drafting of the Building materials decree (BMD) [1, 2, 3]. Around 1990 the results were far enough established to transfer them into a regulatory framework, although many detailed questions were still unanswered.

2. DEVELOPMENT OF JUDGEMENT CRITERIA FOR CONSTRUCTION MATERIALS

In the development of *judgement criteria* for construction materials in the last two decades, a large part of the work was dedicated to the development of the BMD. Another part of the work was the implementation in other areas of environmental regulation, as well as for discussions in CEN committees, e.g:

2.2 Environmental criteria for construction materials used in the process of development of the BMD or other relevant environmental legislation

- *Building materials decree (BMD):* The decree was especially developed for giving criteria to protect soil (soil/sediment and ground water) when using material in construction. Attention was focussed on the release of components from materials due to contact with water. The use of building materials inside a building is excluded from this decree.
- *Health*: Health aspects, due to dangerous substances in construction materials, are governed in several specific regulations, e.g. radon, asbestos, PAH.
- *Labour safety*: Several safety regulations cover dangerous substances, e.g. volatile organic carbons (VOC), asbestos, PAH.
- *General policy and regulations on dangerous substances*: This policy prevents dispersion of dangerous substances into the environment. This policy is based on general health risks and general ecological aspects.
- *Waste materials*: The policy is aimed at decreasing the amount of waste materials that need to be disposed of on waste disposal sites. If disposal is still necessary, adequately designed and managed waste disposal sites have to be realised. In general, management is based on the policy of priority setting in the order of a decreasing priority of applications. However, prevention of the production of waste materials is looked upon as an overall policy measure. Starting with product re-use, the following options are taken into account: material re-use, beneficial use, disposal or re-use with energy recovery and landfilling of waste. Recently, national decrees were introduced, forbidding the dumping of many kinds of waste materials on waste disposal sites. Producers of these waste materials have to first find other solutions, following this priority list. Closed chain management should be followed as much as possible. Materials should be re-used as often as possible.
- *Sustainable development in construction*: A new policy approach, which is based on measures taken by the companies by free choice. However, parts of this policy will be inserted step by step into general regulations, depending on the results of market developments.

From this (incomplete) list it may be concluded that nowadays in the Netherlands a great number of environmental aspects have to be paid attention to while developing, producing, using, recycling and disposing of construction materials. For the EU-Construction products directive (CPD), in 1999 an inventory was made of all national Dutch regulations concerning dangerous substances and which were fully or partly governing all kinds of construction materials. About 40 to 50 regulations proved to be dealing with construction products. Thus the BMD is one of a great number of regulators the construction industry has to deal with. In general the BMD is one of the more 'important' regulations in this field because its working area is very broad, the procedures for testing have been worked out in detail, and for many products the BMD is the beginning of a product certification process.

2.3 Primary, secondary and waste materials

In the BMD and in many other environmental regulations there is no distinction between these three types of materials. All these materials have to meet the same standards. In general there is no difference in the way materials are tested. If the matrix of materials is more or less the same, the same testing procedure can be used for examining the quality of the materials, independent of the status 'primary', 'secondary' or 'waste material'. After going through such a test scheme, a conclusion can be made as to whether a material can be re-used, treated, or disposed of. For secondary materials it is important that they are dealt with in the same way as primary materials. This is the only way to provide opportunities in marketing them in the construction industry. It is important that in standardisation of documents, legislation, etc. no discrimination is made in the use of primary or secondary materials or waste materials. When materials meet the basic quality criteria, it must be possible to utilise them.

There is only one specific place where differences are made in primary, secondary and waste materials, namely in waste management acts and regulations. The difference between these terms is not based on the difference in quality, but mainly on the question 'if' and 'how' waste materials need to be managed and controlled to be sure they are properly handled. After adequate treatment and testing most of these materials can be finally re-used as normal materials.

3. ENVIRONMENTAL RULES WITHIN THE BMD-FRAMEWORK

3.1 General soil protection standard setting.

In the complex matter of standard setting in soil protection, some main points were important for the development of the BMD. Soil protection policy in The Netherlands is based on the principle of "multifunctionality of the soil". This implies that a clean soil has to be kept clean and a polluted soil should not be polluted any further, but must be improved as far as possible in all cases of human usage. 'Target values for clean soil' are defined as a reference for describing a clean soil in policy making. These values are based on data obtained by analysis of unpolluted soil and data of negligible risk for human exposure and ecological quality.

"Intervention values" beyond these target values have also been developed, especially if judging of soil pollution is detected in practice. When the level of a pollutant exceeds this intervention value, in general restorative measures have to be taken by the owner of that piece of land within a short term [10].

3.2 General policy on standard setting for land based activities in soil prevention decrees

As mentioned, the target values and the intervention values have been based on risk assessment. Pollution of the soil should be as low as possible, and when possible without any burden at all. If this is not possible and the activity at the location cannot be forbidden (for social or economical reasons) according to the general soil protection policy, the pollution load into the soil should be 'As Low As Reasonable Achievable' (ALARA). In fact ALARA means that state of the art technology is applicable in all situations, including soil protection. The initial quality of the soil on which the activity takes place does not influence this basic principle. So on polluted soils the environmental load should be equally minimised. If for a certain activity burdening of the soil or surface water cannot be avoided, often a maximum level of the burdening is defined, or certain preventive measures are demanded. As far as possible these levels or measures must be determined in such a way that it is expected that the quality of soil/sediment and groundwater will not exceed the target values. In general, it is obvious that activities should not result in a polluted soil, which has to be cleaned up afterwards.

3.3 Setting of standards

A maximum level for the release of inorganic substances from construction materials was based on the principles mentioned above. This level was transferred into an 'immission value'. A 'marginal burdening' is excepted when it does not exceed a level of 1% of the concentration of the target value of an inorganic substance in 1 meter of the soil within a period of 100 years. With this theoretical approach it is expected that the sediment and the groundwater are sufficiently protected and that the continuty of the use of most of the primary and secondary materials remains possible. For a number of materials technical improvement is required for the continuation of the usage of these materials.

For inorganic substances no maximum concentration levels have been defined. It is expected that construction materials will not be mixed within the soil during construction and during the lifetime of the construction. Polluted soil may be used as a 'construction material', e.g. for embankments or road construction. If polluted soil is used, it has to meet the immission levels (marginal burdening) and the concentration of inorganic and organic components have to remain below certain maximum levels (mostly below the intervention values). The setting of a maximum concentration level is necessary as a preventive measure because there is a great risk that at a certain time the polluted soil becomes mixed with the surrounding soil.

The development of test methods and the insight into release mechanisms have not yet advanced as far as they have for inorganic components. For volatile organic components it is impossible to develop useful test methods because the speed of release depends on the local situation. Moreover, during sampling of the soil and testing in laboratories an unknown part of the organic components may disappear, thereby making the results unrepresentative.

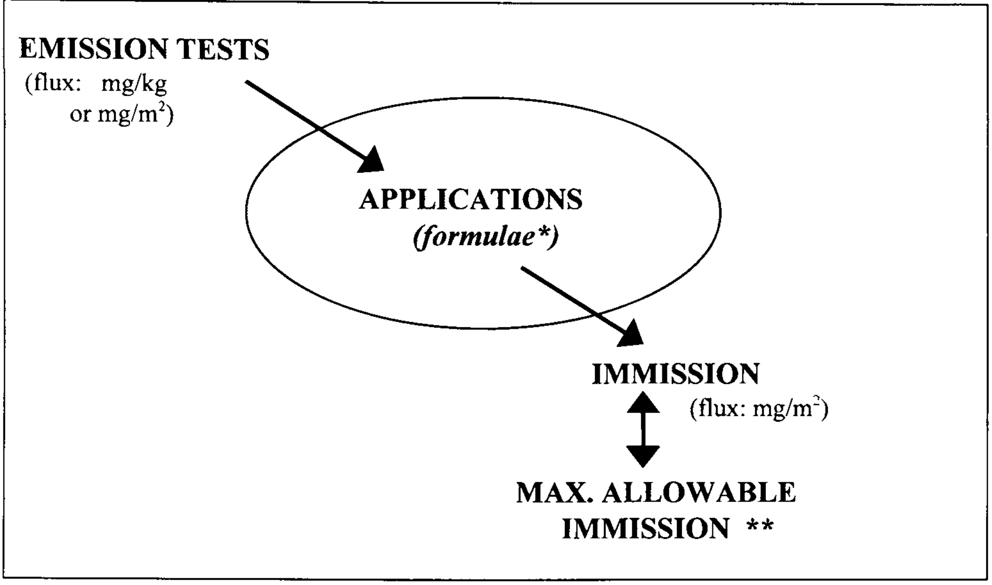
In general, a small number of non-volatile organic materials are expected to be present in a relatively small number of construction products. When technical developments of testing methods have reached an acceptable level, it could be considered to add these release tests to the regulations for a selected group of organic components. For other organic components only a test on the total amount remains possible. It also has to be taken into account that for some organic components, such as PAH, there are other environmental regulations on dangerous substances limiting the maximum content of these components. Based on these observations, a release test for organic components has not yet been introduced into the BMD and other regulations.

3.4 Calculation of emission values (fig. 1)

Emissions are measured in the laboratory by means of advanced release tests: a column test for granular material; a diffusion test for moulded materials and for monolithic materials. It has proved to be too expensive, complicated and time consuming to test materials in field situations.

A formula was developed to make a correlation between the emission test results and the maximum immission values. With this formula it is possible to make a distinction between products in thick layers and products which are used in thin layers, for which the acceptable emission levels are higher. It is also possible to make a distinction between products that can come into contact with water and products that are used in isolated conditions. In these isolated conditions the normal characteristics of certain suitable constructions (e.g. asphalt roads) are used as an isolation cover (infiltration reduction) in combination with additional technical measures, such as a minimum distance above the ground water table [8, 11].

Fig.1. Evaluating construction materials in the Building materials decree



**** = factors in the formulae for the various applications/situations are:***

- *-L/S*
- *-contact time*
- *-isolation*
- *-granular or moulded(stabilised)*
- *-release pattern*
- *-height*
- *-temperature*

***** = basis for standard setting of immission values are:***

- *Target values soil protection)*
  'marginal burdening'
- *ALARA*

3.4 Organic components

At this stage, only maximum concentration levels have been defined for organic substances.

3.5 Prevention of pollution

As mentioned before, the principals of the BMD make it possible to use polluted soil or sediment as a construction material. However, in The Netherlands policy is aimed at cleaning up polluted soils. During recent years the number of known polluted locations has increased dramatically. In many locations construction activities were planned so it became impossible to first fully clean up all those locations. A new strategy is under development in which remediation activities may be planned step by step. This often means treatment as far as necessary for a certain kind of usage, followed by after care measures, as long as the pollution has not been fully cleaned up. It is also accepted that polluted soil is transported and used in another location with a similar soil quality, provided that the usage in that location is monitored by the local community and when enough care is taken to handle the soil in a careful way. Many local communities have introduced a system for soil management. The BMD will be tuned in with the other developments on this point.

3.6 Tools for testing

As mentioned earlier, a lot of attention has had to be paid to test methods and the standardisation of these methods. In co-operation with the Netherlands Standardisation Institute (NNI), a lot of work has been done to develop an adequate set of testing procedures. These methods had to meet the following conditions:

- Giving adequate information about release or content of substances.
- Measuring on a level that could meet rather low concentrations, necessary in relation to the maximum permitted emission levels.
- Unambiguous test results.
- A good performance, repeatability and reproducibility.

Furthermore, it is necessary for the application of these methods by industry to develop a complete testing procedure, from sampling to reporting the final data. For this purpose, a modular system of test methods has been developed and issued as Dutch Standards by the NNI [6]. To assure that these methods will be properly used, a system of quality assurance has also been developed. Laboratory and 'sample takers' have to get an *accreditation*, based on a specially developed accreditation program for the BMD. Only laboratory and 'sample takers' in possession of this accreditation may perform tests for the industry or government institutions within the framework of the BMD.

This whole system appears to be complicated and heavy. It requires much more attention by the laboratories and other organisations concerned than they previously invested in these kinds of measurements. The results of these new procedures proved to give a higher quality of data than before, e.g. when starting these developments it was often supposed that sampling would always give a much lower precision than other steps in the analysis of the quality of the products. It was often said that better results in sampling should not be reachable and should not be predictable very well. From recent experience it becomes clear that a consequent execution of those new techniques and procedures can lead to much better results. The precision of sampling can get on the same level as the (increased) precision of other steps in the measuring procedures.

3.7 Certification and accreditation

As indicated before, it was felt necessary to take a number of measures to make it possible to realise the safe use and re-use of materials. To be sure, this will be done in a proper way; it is necessary to pay enough attention to enforcement of the rules by local authorities. It was therefore felt necessary to introduce *certification* for construction products, to improve effectiveness and efficiency of enforcement. Certification is a means of ensuring products are in compliance with legal standards. A special guideline was made for the working out of the certification procedures [4]. A number of pilot projects on certification of varying products were executed. Finally, it took more time for industries to prepare certification for all the important (groups of) construction products. On 1 July 1999 it was decided to give industry more time to finalise its certification. A special temporary regulation was made for those industries that could prove that they had made progress in preparing certification. It is expected that most of industries can finalise the certification procedures before 1 July 2000.

When a producer or a user can show an official certificate on the quality of a construction product, the local authority must accept this as 'sufficient proof' of quality. The local authority is not allowed to ask for more information or reports, etc. If the authority wants an (extra) check on quality, it has to execute and to pay for the costs of these measurements itself. For such a check he can make use of the special protocols for enforcement testing. If a construction product is then not yet certified, it should be tested, batch by batch. This testing has to be executed with the special protocols on testing soil/sediment and on other construction materials [3].

3.8 Construction products in surface water.

In the process of the development of the testing procedures within the BMD-framework, the use of *building materials in surface water* and the judging of these applications was included in the decree. It proved to be possible to do the evaluation in the same way as has been developed for land based applications. This made it possible to include this type of application in the further development of the decree itself. In daily practice it is comfortable that the same procedures can be used.

3.9 Some other points of attention

In relation to the use of the results of release tests in evaluation of applications of construction materials, the results are expressed as a *load*: in mg/kg when using the column tests or in mg/m^2 when using the diffusion tests. It is not important to know the concentration in the eluate because concentration varies with the quantity of the eluate that is being used in the laboratory test. With the release load, however, a relation can be made with the soil protection criteria as outlined above.

A number of *basic characterisation* tests have been developed. Some of them have been chosen for *general judgement of a material* within the BMD-framework; when using these basic tests a judgement can be made for a wide range of products. For daily testing in industrial production circumstances, simplified *compliance test procedures* for individual products may be used, provided that these have been verified in a certification scheme. Such schemes have to comply with national and European requirements and procedures.

4. PARTIES INVOLVED IN THE DEVELOPMENT OF THE BMD

From 1980 to 1990 several institutes and laboratories worked together to develop testing methods and to derive scientific insight into the mechanisms of the release of various components. The preparation of the BMD by the Dutch Government started around 1990. The field of work was broad and complex and there were many interests for society and industry which had to be considered in this decree. Several questions had to be answered within the accompanying research program, but it was felt necessary by the Government that more clarity could be given to all relevant parties on the criteria for the safe use and re-use of materials in construction. Because of the expected impact of the decree on society, the Government stimulated relevant parties to become involved in the developing process. The results of the laboratory work on the development of testing procedures and derived data of various materials, as well as the outlines of the decree, have been discussed periodically with a group of representatives from industry and with a group of representatives from local and regional authorities. From these discussions, special points of interest to be taken into account were:

Industry: Will the products for construction meet the proposed levels; opportunities and costs of quality improvement; (extra) costs introduced in the production process and the costs of certification of the products; possible changes in compatibility between products and producers; adequate information for individual industries and the relevance of international developments.

Laboratory: Quality and uniformity of test results; accreditation of laboratories; costs of testing and compatibility.

Communities / provinces and boards for water-management: Enforcement of regulations; certification of the construction products; costs of enforcement; information to the public and all parties concerned.

Parliament: Development of policy on waste management, sustainability, dangerous substances, soil protection, costs and results of these regulations; possible changes in compatibility between producers and the relevance of European and international developments.

Several co-ordinating organisations from industry and companies, laboratories and authorities, were highly involved in the process of the development of the decree. Environmental organisations critically followed the process as well. By being involved in the development many of these parties were able to participate in various ways in these developments. Other parties decided to wait until the developments were almost finalised and for the decree to be implemented into legislation. For the latter it will be more difficult to meet the new standards in time. For them it will be difficult, too, to get a good integrated insight into the whole field of environmental regulations, of which the BMD is one of the more important pieces of legislation.

5. DOCUMENTS AND INSTRUCTIONS PRODUCED ACCOMPANYING THE BMD

Within the framework of the BMD several documents and instructions have been prepared. This was necessary because of the complexity of testing procedures, the certification process and also as background documents for industry. In the process of implementing the decree into society, the transfer of knowledge and know-how is an important aspect. Moreover, these documents were also used for discussions in European circles and CEN committees. The main documents available for parties in the Dutch society are:

1. The Building Materials Decree (1995) [1, 2]
2. The Ministerial decision based on the BMD (1996), including several supplements containing, amongst others, technical specifications and protocols for the examination of the content of substances, the emissions and immissions of substances and isolation measures. [3]
3. A dispensation regulation based on the BMD (1999), containing temporary special dispensations for some industries or construction products, necessary because of awaiting technical developments or final specific alterations of the BMD.

For the proper execution of the regulations a number of formal instructions have been developed, of which the most important are:

1. Enforcement protocol 1999
2. Accreditation programs on:
    - sampling
    - laboratory testing:
        - concentrations of components
        - release of components
        - guidelines for calculations

A number of documents and guidelines have been produced for the support of an adequate and clear execution of the decree:

1. Certification assessment guideline for building materials [4]
2. Guidelines for local authorities supporting enforcement of this regulation [7]
3. Leaflet with the main points of the BMD [2]
4. Handbook for industry, designers and contractors [5]
5. A floppy disk with a knowledge based program

In order to make it possible for parties to obtain information regarding the decree and the methods for implementing the requirements in the various situations applicable, an accompanying program for transfer of know-how has been put into action, consisting of:

1. Helpdesks where individuals, companies and local authorities can make telephone inquiries for information (Infomil: +31-70-3610575; RWS/DWW: +31-15-2518205)
2. Courses and symposia: specialised courses for different groups have been organised.
3. A special chapter on the internet website of the Ministry of Housing, Spatial Planning and the Environment (www.minvrom.nl/milieu/bodem). This website gives access to the text of regulations, reports and background information on materials and construction materials. A special chapter for English translations of these regulations and reports is under development.

6. IMPLEMENTATION OF THE BMD IN SOCIETY

Recently much attention has been paid to the implementation of the process of certification of construction products and to the realisation of adequate enforcement procedures by local authorities, who have been given new tasks formerly executed mainly by the provinces. The aim of the latter change has been to implement control schemes in an efficient way and because of the fact that industrial activities and the legislative field of construction are already the task of local authorities. Effects of the decree in society will be monitored for two years and then reported back to Parliament. Furthermore, a number of remaining questions will have to be solved during this monitoring and evaluation phase of the legislation. Additional research programs have been put into action and the results of these activities may have to be implemented by updating existing test procedures or, in the case of organic components, by introducing additional procedures.

Because of European rules, attention has to be paid to European and other international developments, especially in relation to the EU-Construction Products Directive and the EU-Directive on the Landfill of Waste Materials. The Technical Specifications of the EU-CPD will mainly be developed within the framework of CEN. Therefore co-operation in CEN and in the EU is important in order to develop practical procedures with a high quality and a wide field of application with respect to materials and production methods. From the Dutch point of view, based on experiences with the development of the BMD, it would be much better to develop regulations and testing methods in a 'horizontally' oriented way. This way they can be used in all fields of construction and other materials, while the development of different methods in each separate field of construction products results in a non-consistent situation for industry and consumers. Besides the fact that this would be counterproductive in the field of research and development, it will be very counterproductive in (environmental) legislation and lead to a situation where effective cost control in the testing of building materials is hampered.

7. SUMMARY AND CONCLUSIONS

Soil pollution due to leaching of construction materials, either produced from primary feed stock materials or based upon recycling of secondary materials in The Netherlands, has been greatly improved by the implementation of the Building materials decree (BDM). The process of the development of the decree, with all its accompanying regulations and guidelines, has been a very complicated matter in relation to the primary purpose defined at the start of discussions in society. However, because much attention has been paid to the development of new or improved instruments for the successful execution of this regulation (such as test methods, quality improvement of laboratory test results, certification schemes and accreditation of parties involved in the execution of control measures), the final results are acceptable to both the construction industry and the Government.

A very important step in the process has been the involvement of industry, companies, laboratories and organisations representing institutions in the discussions of standard setting and the definition phase of management and certification schemes. This regulation, with all its new instruments, is an important element in the creation of a coherent policy for the management of construction materials, in view of developing a sustainable society. Specialists from both industry and governmental institutions have to keep themselves involved in the whole field of materials, waste management and environmental policy. This enables society to obtain the best results in terms of environmental quality, thereby making it possible that overall costs can be decreased. From a governmental point of view, from experience with the chosen process for developing the decree it is concluded that the involvement resulted in a better motivation of all parties with this integral approach.

Furthermore, the coherently managed research program accompanying the development of the decree resulted in data on materials, knowledge, and instruments that can be used in other environmental fields too. The test methods and certification procedures can also be used for better management of waste materials, including treated and stabilised waste materials that will be disposed of on waste disposal sites or used in special civil applications. Environmental enforcement activities can be executed more efficiently by integration of the enforcement activities for several different environmental regulations, all having effect on one branch of industry or one group of materials.

The results of this development in The Netherlands may be of importance to countries, which are still in the process of developing legislation with respect to soil pollution and leaching of construction materials. As far as the European activities in this field already in operation, results obtained so far in this program, or results from new running programs, will be brought into discussions. Because various Dutch organisations, both industrial and governmental, participate in CEN committees, a great part of the data obtained is directly brought into discussions about and development of standardisation in Europe.

Some main points of the Dutch experience are summarised below:

- Development of life cycle management and sustainability in the field of materials for construction requires clear criteria. In this respect important steps have been set in the BMD.
- In the development of test methods and environmental standard setting, no differences should be made between primary materials, secondary materials and waste materials. The

procedures for testing and judging can be the same, as is demonstrated in the Dutch approach where the results of test procedures basically determine the way the materials will be used and handled further, either as a construction product or as a waste material.

- Understanding the chemical and physical mechanisms of the release process (leaching) is crucial in order to develop adequate test procedures. For the Dutch situation, there is enough knowledge available in the form of data on construction materials to use the testing procedures for legislative purposes.
- It is important that research and development should be carried out in international co-operation.
- The quality and uniformity of the execution of laboratory tests and the accreditation of the laboratories is necessary for implementation of the legislation in such a way that costs for the industry and society are in balance.
- The certification systems which have been worked out in several countries should be further improved and integrated internationally.
- A main part of waste materials can be safely reused, if thoroughly treated in all aspects.
- In standardisation of products, no difference should be made to the origin of the raw materials, but only in the quality, based on the same test methods.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Chemical-Mineralogical Valuation of the Leachate Potential of Municipal Solid Waste Incineration (MSWI) Bottom Ashes

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Within the framework of a research project mineralogical, chemical and structural engineering methods were applied to raw bottom ashes as well as to processed bottom ashes stored for three months, all originating in 15 German municipal solid waste incineration plants operated on different process technologies.

The chemical analysis showed that bottom ashes contain silicon, aluminum, iron and calcium as the principal elements. Titanium, manganese, sodium, potassium and phosphate occur in addition. Traces of barium, strontium, rubidium and the heavy metals copper, zinc, lead, chromium, nickel and cadmium are present. Accordingly, MSWI bottom ash is a calcium-aluminum silicate mixed with an iron fraction. The anions detected are mainly chloride and sulfate with lesser concentrations of fluoride.

The concentration of harmful products in the bottom ashes is no measure of the environmental risk (polution potential). The environmental impact depends upon the present minerals, the stage of alteration and the mobility or leaching properties of the component in question and thus is mainly controlled by:

- the speciation
- matrix band (fixation in the matrix)
- the alkalinity of the material
- the actual pH of the leachate
- the complexing properties of the leachate
- the temperature

In order to characterize the solution behaviour the following 3 leaching tests were applied:

- the German DEV-S4 test is used for the comparative evaluation of the environmentally relevant properties of industrial by-products
- the column test is used for the determination of the short- and medium-long term leaching behaviour
- the availability test is used to determine the maximum leachability for each of the components of the bottom ashes

1. MINERALOGY

The MSWI bottom ashes are a multi-component system of slag fractions, glass, ceramics, metals, other constituents (e. g. rock) and unburned residues.

With a view to the crucial structural engineering and environmentally relevant properties of bottom ashes the mineralogical composition of the largest group of materials, the slag fraction, commands particular interest. The crystalline structure and the types of bond of the crystals in the mineral phases present are responsible for the physical and chemical properties of a material.

The MSWI bottom ashes consist mainly of silicates, oxides and carbonates. Secondary phases occuring are amorphous glass phases, several iron minerals and feldspars. Accessory and trace substances detected include metals, alloys as well as a great variety of sulfates.

At the formation process of the grate ashes in the combustion chamber no thermodynamic balance appeared with respect to the primarily formed mineral phases. This means, after discharging from the combustion chamber via a quench tank the primarily formed raw bottom ashes (Table 1) are not thermodynamically stable products according to their mineralogical composition. They undergo under ambient conditions with respect to their mineral composition further mineralogical processes. In the first three months of storing mineralogical alteration processes (hydration reactions, solidification reactions, sulfate reactions, salt formation reactions, reactions of iron and aluminum, solution reactions) take place (Fig. 1) and stable bottom ashes (Table 2) were formed. After three month of storing it is possible to use the bottom ashes as material for road construction (unbounded and hydraulically bounded material). This means the mineralogical processes determine the environmentally relevant and the structural engineering properties of MSWI bottom ashes.

2. CHEMICAL COMPOSITION OF MSWI BOTTOM ASHES

A comparison of the chemical bulk composition of MSWI bottom ashes expressed in terms of weight concentrations of oxides shows that the contents of the principal elements silicon, calcium, iron and aluminum have larger ranges. In the first place these differing ranges of the bulk composition can be refered to the different waste input as well as alteration reactions. The elements silicon, calcium and aluminium build up the mineral phases which represent the main mineralogical composition.

Table 1
Mineralogy of Raw Bottom Ashes

Phase	Formula	A	B	C	D	E	F	G	H	I	J	K	L	M
Glass		x	xx	x	x		x		x	x		x	xx	x
Quarz	SiO_2	xxxx	xxxx	xxx	xxxx	xxx	xxxx	xxxx	xxxx	xxxx	xxxx	xxx	xxxx	xxx
Gehlenite	$Ca_2Al_2SiO_7$	xx	xx	xxxx	xxx	xxx	xxxx	xxx	xxx		xxx			
Akermanite	$Ca_2MgSi_2O_7$	xx	xx		x					xxx		xxx	xxx	xxx
Calcite	$CaCO_3$	xx	xxx	xx	xxx	xxxx	xxxx	xxx	xx	xx	xx	xx	xx	xxx
Magnetite	Fe_3O_4	xx		x	xxx	x		xxx	xxx	xxx	xxx	xxx	xxx	xxx
Maghemite	γ - Fe_2O_3						x							
Haematite	α - Fe_2O_3	xx	xx	x			x							
Marcasite	FeS_2			x	xx	xx	xx	xx	xx	xx		xx	xx	xx
Kalifelspar	$(Na,K)[AlSi_3O_8]$	xx		xx	xx	x	xx	xxx	xxx	xx	xx	x	x	x
Plagioclase	$(NaAlSi_3O_8-CaAl_2Si_2O_8)$	xx	xx	x	x	xx	xx	xxx	xx	x	xxx	x	x	x
Anhydrite	$CaSO_4$	x		xxx	xx	xxx	xxx	xx	xxx	xx	xxx	xx	xx	xxx
Bassanite	$Ca SO_4x0,5H_2O$				x			x	x	x		x		x
Portlandite	$Ca(OH)_2$	x		xxx	x	xx	x	x	xx	x	x		x	x
Halite	$NaCl$	x		x	x	xx	xx	x	xx	x	xx	x	x	xx
Sylvite	KCl	x		x			x	x		x			x	x
Magnesite	$MgCO_3$			xx	x	x	x					x	x	
Siderit	$FeCO_3$			x	x		x							
Apatite	$Ca_5[(F,Cl,OH)(PO_4)_3]$		xx		x		xx					x	x	x
Diopside	$Ca(Mg,Fe)(Si_2O_6)$	xx		x	x	x		xxx	xx	xxx	xx	xx	xx	xxx

- Hydratation reactions (fast reaction)
- Solidification reactions
  - ⇒ portlandite to calcite

$$\underset{\text{portlandite}}{Ca(OH)_2} + CO_2 \rightarrow \underset{\text{calcite}}{CaCO_3}$$

  - ⇒ Direct precipitation of calcite
  - ⇒ Formation of calcium silicate hydrate phases (CSH)?
- Sulfate reactions
  - ⇒ Conversion: anhydrite to bassanite

$$\underset{\text{anhydrite}}{CaSO_4} + \tfrac{1}{2} H_2O \rightarrow \underset{\text{bassanite}}{CaSO_4x0,5H_2O}$$

  - ⇒ Direct precipitation of bassanite
- Salt formation reactions
  - ⇒ halite (NaCl), sylvite (KCl)
- Reactions of iron (slow reactions)

$$\underset{\text{magnetite}}{Fe_3O_4} \rightarrow \underset{\text{maghemite}}{\gamma\text{-}Fe_2O_3} \rightarrow \underset{\text{haematite}}{\alpha\text{-}Fe_2O_3}$$

- Decomposition of marcasite (FeS_2)
- Reactions of aluminum
- Solution reactions

Figure 1. Major mineral reactions taking place during the first three months of storage

Table 2
Mineralogy of Processed and Stored MSWI Bottom Ashes

Phase	Formula	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Glass		x	x		x	x	x	x	x	x	xx	x	x		x
Quarz	SiO_2	xxxx	xxxx	xxxx	xxxx	xxxx	xxxx	xxx	xxxx	xxxx	xxxx	xxx	xxxx	xxxx	xxxx
Gehlenite	$Ca_2Al_2SiO_7$	xx	x	xxx	xx	xx	x	xx	xx	xx	xx	x			
Akermanite	$Ca_2MgSi_2O_7$	x	xxx		x		xxx	x	x	x	xx	xxxx	xxx	xxxx	xxx
Calcite	$CaCO_3$	xxx	xxxx	xxx	xxx	xxx	xxxx	xxx	xxx	xxx	xxx	xxx	xxx	xx	xxx
Magnetite	Fe_3O_4	x	xx	xxx	xxx	xx	xx	xxx	xx	xx	xxxx	xxx	xxx	xxx	xxx
Maghemite	$\gamma - Fe_2O_3$	x		x	x	x		x		x	x				
Haematite	$\alpha - Fe_2O_3$				x	x						x	x		
Marcasite	FeS_2	x	xx	x	xx	xx	xx	xx	x	xx	x	xx	xx	xx	xx
Kalifelspar	$(Na,K)[AlSi_3O_8]$	xx	xx	xx	xx	xxx	xx	xx	xx	xxx	xxx	x	x	x	xx
Plagioclase	$(NaAlSi_3O_8\text{-}CaAl_2Si_2O_8)$	xx	xx	xx	xxx	x	xx	xx	xx	x	xx	x	xx		xx
Anhydrite	$CaSO_4$		x	xx			x	x	xx	x	x	x	x	x	x
Bassanite	$Ca\ SO_4x0,5H_2O$	xx	xx	x	xx	xx	xx	x	x	xx	xx	xx	xx	xx	xx
Gypsum	$CaSO_4x2H_2O$											x			
Portlandite	$Ca(OH)_2$		x				x					x	x	x	x
Halite	$NaCl$	x		x	x		x	x	x	x	x	x	x		x
Sylvite	KCl											x			x
Magnesite	$MgCO_3$	x	x		x	x				x		x	xx		
Siderit	$FeCO_3$		x				x								
Apatite	$Ca_5[(F,Cl,OH)(PO_4)_3]$	x	x		xx	x	x			x	x	x			
Diopside	$Ca(Mg,Fe)(Si_2O_6)$	x	xx	xx	x	xx	x	xx	xx	x	xx	xx	xx	xx	xxx

The mineralogical composition of MSWI bottom ashes and the contents of the principal elements deviate from the contents are found in natural rocks and industrial by-products such as blast furnace slags or electro oven slags. MSWI bottom ashes differ from acidic magmatites (silica concentration: 66 or more wt.%; granite, rhyolite) due lower SiO_2- and higher CaO contents, but have a similar chemical bulk composition to basic magmatites (silica concentration: 45 to 52 wt.%; gabbro, diabas, basalt, nepheline). However, the CaO contents of the MSWI bottom ashes are higher accordingly to the acidic magmatites. The blast furnace slags differs from the MSWI bottom ashes in the first place through higher contents of CaO wheres electo oven slags shows higher contents of CaO and lower contents of SiO_2 (Fig. 2).

3. ELUTION BEHAVIOUR

The concentration of harmful products in the MSWI bottom ashes is no measure of the envirionmental risk (polution potential). More important for the environmental impact are the leaching properties and the mobility of the components out of the mineral phases

The elution behaviour of MSWI bottom ashes from 15 municipal solid waste incinerator plants operated on different process technologies is characterized by the following 3 elution tests:

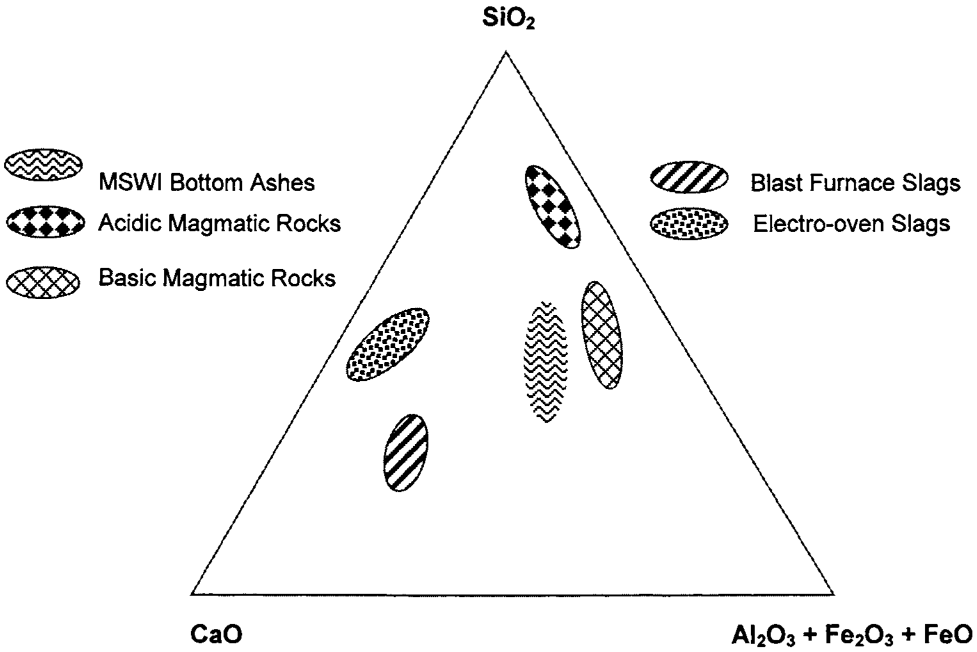

Figure 2. Chemical Composition of MSWI Bottom Ashes

- the German DEV-S4 [1] test is used for the comparative evaluation of the environmentally relevant properties of industrial by-products [2] based on the crucial limits of national regulations (e.g. LAGA [3])
- the column test [4] is used for the determination of the short- and medium-long term leaching behaviour
- the availability test [5] is used to determine the maximum leachability for each of the components of the bottom ashes

3.1 DEV-S4 Test

The DEV-S4 test is a non pH controlled extraction test where the sample is shaken in water during the experimental time of 24 hours. The quotient between the volume of water used for the DEV-S4 test and the quantity of testing material is 10.

The statistical interpretation of a quality controlled MSWI bottom ash shows (Table 3):

- The largest fraction of cations in the solution is made up by calcium, sodium and potassium. The anions are sulfate and chloride.

Table 3
Statistical Interpretation of Elution Datas (DEV S4-Process)

		Bottom Ashes from MSW Incineration Plant D					
Parameter	Unit	Samples	Arithmetic Means	Standard Deviation	Minimum	Maximum	LAGA
Calcium	mg/l	28	171	59,2	73	331	
Magnesium	mg/l	28	1,6	2,5	0	8	
Sodium	mg/l	28	99,2	48,6	26	220	
Potassium	mg/l	28	40,4	14,2	17	81	
Iron	mg/l	27	0,19	0,11	0	1,8	
Manganese	mg/l	27	0,015	0,025	0	0,02	
Silicate	mg/l	25	1,43	1,4	0,1	6	
Lead	mg/l	26	0,008	0,01	0,0005	0.037	0,05
Cadmium	mg/l	26	0,0005	0	0,0001	0,0037	0,005
Chromium	mg/l	26	0,038	0,02	0,003	0.088	0,2
Nickel	mg/l	26	0,006	0	0,001	0.022	0,04
Copper	mg/l	26	0,044	0,02	0,01	0,1	0,3
Zinc	mg/l	26	0,034	0,04	0,009	0,2	0,3
Mercury	mg/l	23	0,00014	0,00008	0,00003	0,0002	0,001
Arsen	mg/l	24	0,00018	0	0,00003	0.001	
Chloride	mg/l	28	81,4	30,5	44	170	250
Sulfate	mg/l	28	472	180	230	769	600
Cyanide	mg/l	9	0,02	0	< 0,02	< 0,02	0,02
Hydrocarbons	mg/l	11	0,14	0,05	0,1	0,2	
AOX	mg/l	10	0,029	0,03	0,01	0.083	
Phenole	mg/l	14	0,027	0,03	0,002	0,13	
pH		28	10,4	0,5	9,5	11,4	7 bis 13
el. Conductivity	mS/cm	28	127	26,1	62,9	175	600

- The largest standard deviations are refered to the elements calcium, sodium, potassium, chloride and sulfate. These elements build up the soluble salts halite (NaCl) and sylvite (KCl), the sulfates anhydrite ($CaSO_4$) and bassanite ($CaSO_4 x 0,5 H_2O$) as well as carbonates, e.g. Calcit ($CaCO_3$). The high leaching rates of these elements are attributable to these mineral phases, which react very sensitive of modifications of the physical-chemical environment.
- The arithmetic means of the concentrations of the heavy metals, chloride, sulfate and cyanide are clearly below the crucial limits by LAGA.

3.2 Availability test

The availability test estimates the fraction of the total concentration present, which can be leached under natural conditions in the long term. The availability test is a pH controlled extraction test and works at a pH of 7 (maximum leaching of the soluble salts) and 4 (high leaching rates of heavy metals). Under natural conditions a pH of 4 represent the maximum acidity in natural waters [6].

The test results are (Table 4):

Table 4
Availability Test: Maximum Leachable Quantities in mg/kg

ωES [mg/kg]	K	Ca	Zn	Cu	Pb	Cr	Ni	Sulfate	Chloride
Raw Bottom Ash C	2,37	46,65	1,76	0,08	0,72	0,01	0,02	39,13	3,67
Bottom Ash C	1,99	44,02	1,56	0,12	0,058	0,01	0,02	15,15	3,4
Raw Bottom Ash D	1,96	37,91	0,01	0,2	0,289	0,01	0,01	6,31	4,13
Bottom Ash D	1,25	25,36	0,51	0,09	0,036	0,01	0,01	2,88	3,78
Raw Bottom Ash G	1,32	23,93	0,41	0,08	0,09	0,004	0,005	6,77	2,39
Bottom Ash G	2,36	23,43	0,45	0,11	0,13	0,01	0,01	6,57	2,01
Raw Bottom Ash I	0,62	32,5	0,54	0,01	0,069	0,005	0,02	°	°
Bottom Ash I	1,15	26,89	0,99	0,16	0,063	0,01	0,01	5,28	1,8
Raw Bottom Ash K	1,77	52,81	0,94	0,22	0,075	0,01	0,01	11,37	3,46
Bottom Ash K	1,35	27,57	0,85	0,24	0,53	0,01	0,01	9,71	3,82
Raw Bottom Ash L	1,04	48,89	0,55	0,02	0,007	0,01	0,01	11,78	2,51
Bottom Ash L	2	26,51	1,27	0,32	0,066	0,01	0,01	12,58	7,64
Raw Bottom Ash M	1,03	26,95	0,59	0,15	0,003	0,01	0,01	11,14	0,47
Bottom Ash M	0,69	24,27	0,69	0,26	0,065	0,01	0,01	7,73	5,92
Raw Bottom Ash N	0,48	23,39	0,54	0,05	0,77	0,004	0,01	5,18	1,6
Bottom Ash N	0,37	34,44	0,86	0,12	0,4	°	0,01	11,6	1,82

° no test result

- The highest detected leaching rates has calcium and potassium.
- For the leaching contents of the heavy metals the sequence zinc, lead, copper, nickel and chromium is recognizable

3.3 Column test

The column test is a dynamic flow through test. Increasing volumes of water (pH = 4) flow through the column which is filled with the testing material. Analyses of the eluates at defined quotients between the volume of the water used for the column test and the quantity of testing material results in a temporal splitting of the elution process.

The test results are (Table 5):

- A comparison of elution data (quantity of leached components in % of original content) of raw bottom ashes and bottom ashes of the elements potassium, chloride and sulfate shows no tendency for a reduction or an increase of the elution rates in the first three months of storing. The potentials of elution are constant.
- For the elements calcium, zinc, copper, lead, chromium and nickel a reduction in concentration is observed in the stored bottom ashes. This shows clearly the positive effect of three month storing as regards the environmental compatibility. The reason for this behaviour is a fixation of heavy metals in carbonate structures as well as solution reactions of salt minerals.

Table 5
Column Test: Quantity of Leached Components in [%] of Original Content

U_{ges} [%]	K	Ca	Zn	Cu	Pb	Cr	Ni	Sulfate	Chloride
Raw Bottom Ash C	8,15	0,96	0,076	0,068	0,55	°	0,038	1,51	7,07
Bottom Ash C	13,6	0,87	0,018	0,057	°	0,024	0,039	2,91	6,64
Raw Bottom Ash E	4,2	1,79	0,13	0,18	0,22	0,022	0,72	°	9,41
Bottom Ash E	4,18	1,41	0,022	0,02	°	0,18	0,51	3,14	9,64
Raw Bottom Ash G	3,45	1,21	0,044	0,46	0,042	0,11	0,37	°	9,21
Bottom Ash G	2,16	0,9	0,032	0,035	°	0,047	0,14	1,72	4,78
Raw Bottom Ash H	3,77	2,14	0,12	0,2	0,23	°	0,093	°	4,76
Bottom Ash H	7,97	1,18	0,025	0,048	0,011	0,088	0,3	3,87	7,83
Raw Bottom Ash I	2,84	2,39	0,12	0,05	0,26	°	0,16	2,13	9,18
Bottom Ash I	0,94	0,65	0,014	0,037	0,008	0,023	0,083	°	1,85
Raw Bottom Ash J	8,4	1,58	0,017	0,025	0,58	°	0,09	°	4,24
Bottom Ash J	2,98	1,15	0,021	0,062	0,0026	0,074	0,062	3,6	8,22
Raw Bottom Ash L	°	2	0,036	0,039	0,067	°	0,13	0,83	7,17
Bottom Ash L	8,95	0,26	0,01	0,023	°	°	0,056	0,57	6,63
Raw Bottom Ash M	2,39	0,23	0,004	0,005	0,006	0,037	0,035	°	°
Bottom Ash M	3,3	0,3	0,012	0,002	0,014	°	0,036	0,54	14,89
Raw Bottom Ash N	1,05	1,01	0,037	0,069	0,16	°	0,27	°	3,41
Bottom Ash N	5,01	0,47	0,01	0,12	0,007	0,091	0,12	°	7,15
Raw Bottom Ash O	2,61	4,42	0,22	0,26	0,29	°	0,24	°	°
Bottom Ash O	2,98	1,15	0,014	0,05	0,012	0,045	0,12	3,6	8,22

° no test result

A comparison of the concentrations of the individual eluates of a single column test represented of the MSWI bottom ashes of the municipal solid waste incinerator plant M shows the following test results:

- Calcium, potassium and sulfate shows a strongly reduction of the eluate concentration with an increasing quotient between the volume of the water and the quantity of test material. After increasing contents at the beginning of the elution test chloride shows the same tendency as the other elements. The rapid solution of the readily soluble salts halite ($NaCl$) and sylvite (KCl) as well as the solution of the sulfates anhydrite ($CaSO_4$) and bassanite ($CaSO_4x2H_2O$) are responsible for the described elution behaviour.
- The heavy metals copper, chromium, lead and nickel shows – partly after increasing concentrations at the beginning - a strong drop in the concentrations during the column test. This means high solution rates at the beginning of storage of bottom ashes.

4. SUMMARY

The MSWI bottom ashes consist mainly of silicates, oxides and carbonates. Secondary phases occuring are amorphous glass phases, several iron minerals and feldspars. Accessory and trace substances detected include metals, alloys as well as a great variety of sulfates.

After discharging from the combustion chamber via a quench tank the primarily formed raw bottom ashes are not thermodynamically stable products according to their mineralogical composition. They undergo under ambient conditions with respect to their mineral composition further mineralogical processes. In the first three months of storing mineralogical alteration processes take place and stable bottom ashes were formed.

The mineralogical composition of MSWI bottom ashes and the contents of the principal elements deviate from the contents are found in natural rocks and industrial by-products as blast furnace slags or electro oven slags.

The statistical interpretation of the result of the German DEV-S4 test shows: The largest fraction of cations in the solution is made up by calcium, sodium and potassium. The anions are sulfate and chloride. The largest standard deviations are refered to the elements calcium, sodium, potassium, chloride and sulfate. The arithmetic means of the concentrations of the heavy metals, chloride, sulfate and cyanide are clearly below the crucial limits by LAGA.

The availability test is used to determine the maximum leachability for each of the components of the bottom ashes. The test results are: The highest detected leaching rates has calcium and potassium. For the leaching contents of the heavy metals the sequence zinc, lead, copper, nickel and chromium is recognizable.

The column test is used for the determination of the short- and medium-long term leaching behaviour. The test results are: A comparison of elution data of raw bottom ashes and bottom ashes of the elements potassium, chloride and sulfate shows no tendency for a reduction or an increase of the elution rates in the first three months of storing. The potentials of elution are constant. For the elements calcium, zinc, copper, lead, chromium and nickel a reduction in concentration is observed in the stored bottom ashes. This shows clearly the positive effect of three month storing as regards the environmental compatibility.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Fine cementless concretes from industrial by – products for various uses

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The paper presents technologies of fine concretes for various uses consisting of industrial by-products and containing neither cement nor natural aggregates. The development of the technologies contributes much to the environment preservation, saves natural resources and considerably reduces the cost of buildings. The materials used were by-products from thermal power plants, steel making, abrasive industry, extraction and processing of quartzites and other industries. The work got the prize of the governor of the Kemerovo region, Kuzbass.

1. MATERIALS

1.1. High-Calcium Ash and Slag from Combustion of Brown Coals of the Kansk-Achinsk Basin, Silica Fume

The central part of Siberia is rich in brown coals. Their combustion produces annually millions of tons of ash and slag which are dumped polluting the environment. Meanwhile, as shown by our investigations (1 to 4) , they prove to be excellent materials for producing concretes which are equivalent to cement concretes. In this paper, the fly ash and slag from the Abakan thermal power plant (TPP) are analysed.

Fly Ash. The physical properties and chemical analysis of fly ash from the Abakan TPP are given in Table 1. As compared with ashes from other thermal power plants, this ash has a very low surface area and, in accordance with State Standard (5), should be ground before its utilization (Figures 1 a, b). It has high contents of free calcium oxide (above 5 %) which is bound by silica fume and double thermal treatment using, the technology developed.

Slag Sand. Chemical analysis of slag sand are given in Table 2. To eliminate microcracks and caked ash particles, to enhance its frost resistance, strength and granulometric composition, the liquid slag (10 to 15 % by the ash mass), removed and granulated by water, is ground to sand with a particle size of 0 to 5 mm using the technique developed (Figures 2 and 3 a, b).

Silica Fume. The data on silica fume are given in Table 3. In our work, silica fume was used to: 1) bind free CaO of fly ash during double thermal treatment, thus enhancing binding properties of cementless concrete and preventing destructive processes in it (the effect of expansion in the presence of above 5 % free CaO), and 2) increase the density of concrete owing to its superdispersity.

Table 1
Physical & chemical analysis of fly ash from Abakan TPP

Name of values	Requirement of TU 34-70 for the sorts		Requirement of GOST 25818-91	Data of analysis
	1-st	2-nd	(1-kind)	
Physical characteristics				
Specific surface not less, m^2/kg	280.0	200.0	250.0	235.8
Residual on screen 0.08 % by mass, not more	12.00	15.00	20.00	7.50
Chemical characteristics				
Coefficient of quality Cq, Cq=($CaO+Al_2O_3+MgO+SiO_2$), not less than	1.2	1.0	-	1.13
Content of calcium oxide (CaO), % by mass (main ash),	-	-	10.0	31.20
being high as:				
CaO free, not less than	6.0	9.0	5.0	8.96
Content of magnesium oxide (MgO), % by mass not more	3.0	7.0	5.0	6.31
Content of sulphur - and silphuroxide combinations in count of SO_3, not more	5.0	5.0	5.0	0.86
Content of alkaline oxides in current of Na_2O, % by mass, not more	-	-	1.5	1.10
Loss of mass in calcining (LIC), % by mass, not less	3.0	5.0	3.0	1.85
Oxide of silicon (SiO_2),	-	-	-	39.45
as (SiO_2 free)	-	-	-	24.20
Oxide of aluminium (Al_2O_3)	-	-	-	7.11
Oxide of iron (Fe_2O_3 and FeO)	-	-	-	10.79
Oxide of titanium (TiO_2)	-	-	-	0.90
Oxide of manganese (MnO)	-	-	-	0.18

Table 2
Chemical analysis of slag from Abakan TPP

Name of values	Content by mass, %	
	Requirement of GOST 26644-85	Data of investigation
Oxide of silicon (SiO_2)	without norm	56.47
as in (SiO_2 free)	without norm	15.51
Oxide of calcium (CaO)	without norm	29.92
as in (CaO free)	not more than 1 %	-
Oxide of magnesium (MgO)	without norm	3.50
Oxide of aluminium (Al_2O_3)	without norm	8.16
Oxide of iron (Fe_2O_3 and FeO)	without norm	9.63
Oxide of manganese (MnO)	without norm	0.17
Sulphur - and sulphur oxide compounds in count of SO_3	3	0.01
Oxide of phosphorus (P_2O_5)	without norm	0.05
Losses in calcining (LIC)		
for dense slags	without norm	-
for porous slags	not more than 3 %	-

Table 3
Chemical analysis of silica fume from ferroalloy plant

Chemical analysis	%
SiO_2	85 - 94
Al_2O_3	1.0 - 1.5
MgO	0.8 - 1.2
FeO	1.5 - 2.0
CaO	0.7 - 2.5
$K_2O + Na_2O$	0.6 - 1.5
SO_3	0.3 - 0.5
Loss on ignition	2.3 - 2.5

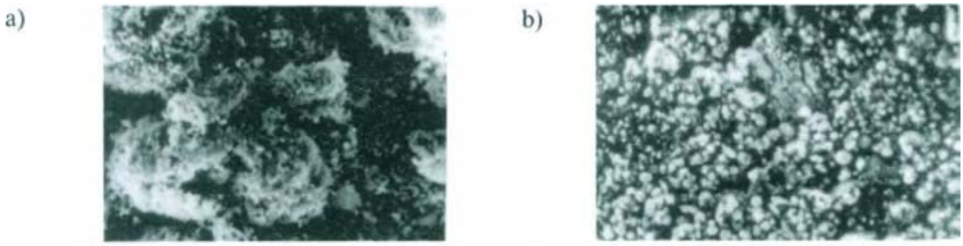

Figure 1. Structure of fly ash from the Abakan TPP
a) before grinding; b) after grinding

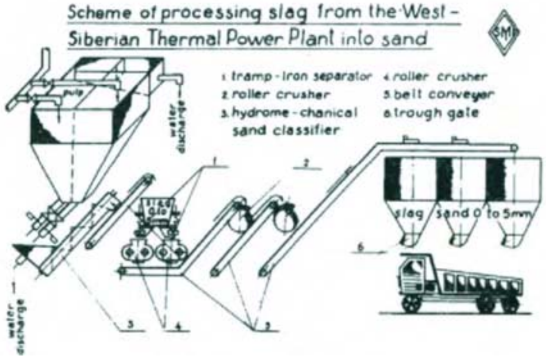

Figure 2. Technological scheme of processing slag into sand

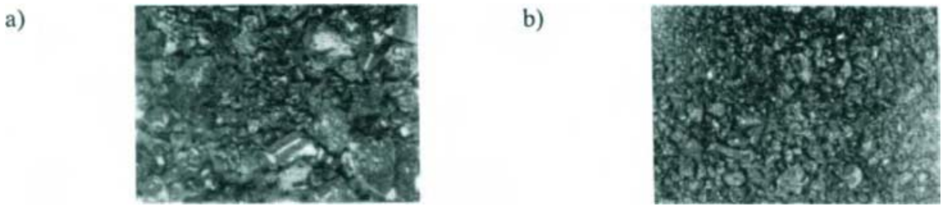

Figure 3. Structure of slag from the Abakan TPP
a) slag before grinding to sand; b) slag sand with a particle size of 0 to 5 mm

1.2. Slags from Steelmaking

Out of 90000 tons of slags produced annually at the Pavlodar Tractor plant (PTP), Kazakhstan, 30000 tons are basis slags and 60000 tons are acidic slags. When ground, basis slag is used as a cementless binder and the acid slag is used as an aggregate. The physical properties and chemical analysis slags are given in Tables 4 and 5. Three types of slags are produced by three different departments.

Table 4
Physical Properties of Slags from PTP

Characteristics of Slag	Slag from SD-1	Slag from SD-2	Cupola Slag
Bulk Density, kg/m^3	1240	1250	1250
Absolute Density, kg/m^3	2450	2750	2800
Crushabilily, %	30	19	13
Cylinder Crushing Strength, MPa	2.44	2.50	2.78
Specific Efficiency, pc/g	0.4	3.1	7.2
Colour	green	yellow-grey	grey

Table 5
Chemical Composition of Slags

Oxides, %	Slag from SD-1	Slag from SD-2	Cupola Slag
SiO_2	30.95	30.06	57.76
Al_2O_3	6.88	2.65	4.40
Fe_2O_3	11.97	1.99	13.77
FeO	8.82	0.71	1.93
CaO (total)	8.95	20.00	10.09
CaO (free)	1.76	4.58	2.12
MgO	11.79	22.34	1.62
Na_2O	1.32	2.34	0.95
K_2O	0.10	0.24	0.58
TiO_2	1.01	0.50	0.85
SO_3	0.43	0.76	0.37
MnO	17.67	18.24	9.59
P_2O_5	0.07	0.06	0.10
Loss on ignition	-	0.13	1.94

Slag from the Steelmaking Department No 1 (SD1). From its granulometric composition, it is referred to as a course sand. It is of a green colour, consisting of particles of various shapes including thin-walled spirals. It has an unstable structure, and after being boiled thrice, it loses up to 50 % weight. It is an acid slag containing up to 20 % iron oxides and metallic inclusions. Therefore, prior to utilization of slag in concrete, it has to be ground to sand, with a particle size distribution of 0 to 5 mm, the magnetic separation should be used to remove metallic inclusions and reduce the iron oxides content.

Slag from the Steelmaking Department No 2 (SD2). It is yellow-grey in colour and consists of lumps 70 mm and larger in size. It loses 12 % weight after being boiled three times. The slag is basic and has good binding properties. The coefficient of quality is more than 1.

$$C_q = \frac{CaO + Al_2O_3 + MgO}{SiO_2} = \frac{20 + 2{,}65 + 22{,}36}{30{,}06} = 1{,}5$$

To make use of its binding properties and prevent its decomposition, it was ground into powder with the surface area of 4000 to 4500 cm^2/g thus releasing free lime and minerals to react with silica and water.

Slag from the Iron Foundry Department (IFD). It is an acid slag which is referred to as a coarse sand from its fineness modulus (3.71). It is ground and subjected to a magnetic separation.

1.3. Industrial By-products for Fireproof Concretes

Quartzite. The Antonovsky quartzite mine of Kuzbass sold the coarse size fraction of quartzite to the Novokuznetsk ferroalloy plant, aluminium plant and two steel Works white the fine size fraction did not have a market and was stored in dumps. Our experimental and industrial tests showed that after washing and grinding, the quartzites from the dumps could be used for refractory materials and products (6, 7). After the reconstruction, a concentrating mill began to supply three desirable size fractions for fireproof concrete (3 to 8 mm, 0,09 to 3 mm and below 0,09 mm).

Technical Grade Liquid Glass. Since conventional liquid glass produced in Russia (State Standard 13073-81) is expensive and far away from the user, the technology for producing technical grade liquid glass from silica fume of the Kuznetsk Ferroalloy plant located near the West-Siberian Steelworks has been developed and tested at a pilot plant of the West-Siberian Steelworks. The technology was based on direct solution of silica fume in sodium hydroxide. A schematic diagram of the production of the technical grade liquid glass is presented in Figure 4. Silica fume tends to becoming caked and to be suspended in hoppers, while "fresh" silica fume can be sufficiently aerated. Taking this into consideration, the West-Siberian Steelworks and the Kuznetsk Ferroalloy plant supply silica fume in a "fresh state" in hermetic containers equipped with aerators. Dissolving active silica in a concentrated solution of caustic soda took place in a vertical steel apparatus with a mixing device. The reaction lasted 1 hour at 90 to 95 ^{0}C (the temperature should be lower than the boiling point of the mixture). The technical grade liquid glass produced meets the requirements of State Standard 13078-81 for liquid soda glass. The density, SiO_2 content, silicate modulus and Na_2O content were 1.36 to 1.45, 24 to 31, 2.6 to 3.0 and 8.7 to 12.2, respectively. The content of solid insoluble sediment (up to 5 %) was higher than the standard (0.2 %). However, as shown by the investigation, this solid sediment increased the strength and heat resistance of fireproof concrete by 35

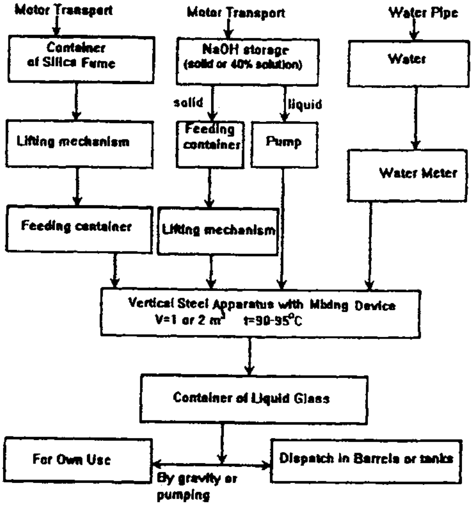

Figure 4. Schematic diagram of the production of the technical grade liquid glass

to 45 and 25 to 30 %, respectively, as compared with concretes containing conventional liquid glass. The technical grade liquid glass exhibited the same binding properties as the conventional liquid glass.

Ferrochrome Slag. Ferrochrome self-decomposing slag from the Chelyabinsk Electrometallurgical Works was used a hardener for the technical grade liquid glass (3 to 6 % by weight of aggregate). This material was taken because of a high content of calcium silicate with rodes mostly in an active form and a low content of impurities. It fell into the program of developing a fireproof concrete from locally procurable materials (quartzite) and industrial by-products (technical grade liquid glass and ferrochrome slag). Unlike other metallurgical slag, ferrochrome slag had high contents of magnesium oxide and very low contents of calcium oxide. The slag contained 27 to 36 % SiO_2, 16 to 22 % Al_2O_3, 3 to 8 Cr_2O_3, 1 to 2 FeO, 38 to 45 % MgO, 1 to 3 % CaO and small amounts of metal. The CaO - to - SiO_2 ratio was 1.7 which provided the formation of $2CaO \cdot SiO_2$. Tasting of the slag showed the necessity of its grinding, classification and separating of metallic inclusions.

2. TECHNOLOGIES

2.1. Fine Cementless Concrete Made of Ash and Slag from the Abakan Thermal Power Plant

As a result of the investigations (8, 9, 10), mixture proportions and the technology of concrete as well as the technological complex project for the processing of high - calcium ash and slag from the Abakan thermal power plant (ATPP) and producing of a cementless binder, cementless concrete, bricks and blocks have been developed. The optimal mixture proportions of concrete are given in Table 6, and the test specimens and the technological scheme for the utilization of the by-products from the ATPP are illustrated in Figures 5 and 6. The complex is under construction at the Abakan TPP. It will be repaid in one and a half year.

Table 6
Optimal mixture proportions of cementless concrete, kg/m^3

Fly ash	Silica fume	Slag sand	Water
615	105	720	480

Figure 5. Test specimens of fine cementless ash - slag concrete

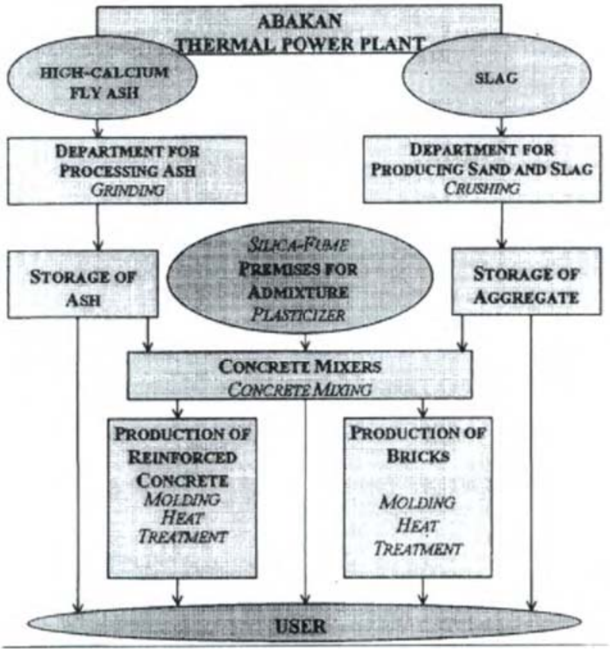

Figure 6. The technological scheme of utilization of Wastes from the Abakan thermal power plant

2.2. Fine Cementless Concrete Made of Foundry Slags from the Pavlodar Tractor Plant, Kazakhstan

Mixture proportions and the technology of fine cementless concrete with basic slags used as a binder and acid slags as a fine aggregate have been developed (11, 12). The mixture proportions and physical properties of this concrete are given in Table 7, and the technological schemes of the production of a binder and slag sand are shown in Figures 7 and 8. Concrete is supposed to be used for the construction of cast in-situ houses and the production of bricks.

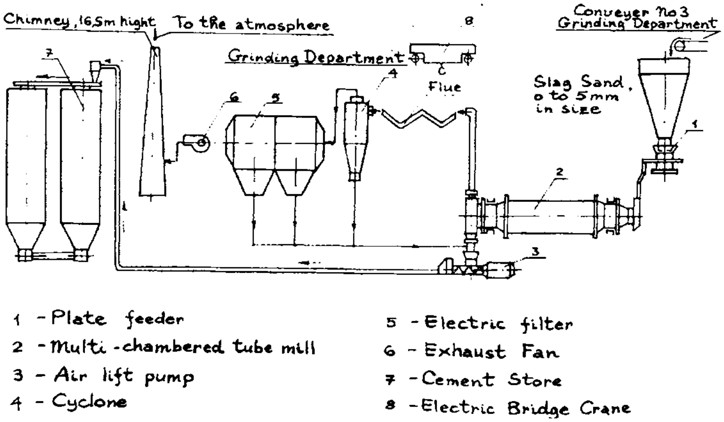

Figure 7. Technological scheme of processing basic slag from the PTP into Binder

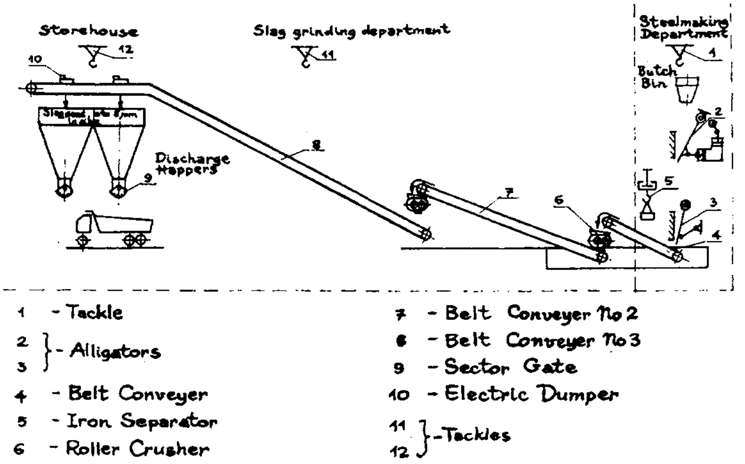

Figure 8. Technological scheme of processing slag from the PTP into sand

Table 7

Optimum Compositions of Fine - Grained Concrete on the Basis of Ground Slag and Slag Sand

Concrete Brand	Ingredients, kg/m^3						Mixture Slump, cm	Average Density of Mixture, kg/m^3	Compressive Strength at 28 days, MPa	Compressive Strength at 180 days, MPa
	Acid Slag Sand SD-1	Acid Slag Sand from Foundry Department	Basic Fine-Ground Slag SD-2	Water	TGL, %	Air-Entraining Admixture, %				
For Non - Load - Bearing Structures										
50	690	-	500	290	0.3	2	4-6	1480	5.6	6.0
50	-	680	520	297	0.3	2	4-6	1497	5.3	5.6
75	765	-	500	295	0.3	1	4-6	1560	8.1	8.6
75	-	750	515	298	0.3	1	4.-.6	1563	7.4	7.8
For Load - Bearing Structures										
100	1077	-	500	278	0.3	-	4-6	1855	10.8	12.0
100	-	1067	510	283	0.3	-	4-6	1860	10.1	11.2
150	1110	-	500	280	0.3	-	4-6	1890	16.2	20.2
150	-	1103	510	285	0.3	-	4-6	1898	15.3	17.4
200	1142	-	500	268	0.3	-	4-6	1910	21.0	25.8
200	-	1140	508	273	0.3	-	4-6	1921	19.7	22.3

2.3. Fine Superfireproof Concrete Made of Industrial Wastes

Mixture proportions and the technology of concretes for the production of blocks for soaking pits (specification 14-3-129-74) (13) and for use in other equipment of iron and steel industry (specification 14-8-184-75) (14) have been developed. Their mixture proportions and physical are given in Tables 8 and 9, and the schematic diagram of their production is presented in Figure 9. A new department is being built for the production of unburut fireproof concretes and concrete products such as blocks, up to 300kg in weight, for lining of walls of soaking pits, small concrete articles for lining of pouring and hot-metal ladles, quartzite blend for chutes of blast furnaces, refractories as well as technical grade liquid glass (TGLG) for foundry and or other purposes. Concrete was tested in soaking pits of the West-Siberian Works. Test blocks served 17 months without thorough repair whereas the dinas blocks made at the Pervouralsk plant usually stand no more than 12 months. The cost of the technical grade liquid glass, quartzite concrete products and fireproof quartzite blend is three times lower than of the conventional materials. The average annual profitability, as determined by the experts from the ministry of Economics, RF, is 43 %, the recoupment of the capital investments is 2.3 years.

Table 8

Properties of concrete as compared with specification 14-8-129-74

Characteristics	Value	
	Specification	Concrete developed
Chemical analysis (%)		
SiO_2, not lower	92	94
$Na_2O + K_2O$, not higher	2.5	1.9
Fire resistance (^0C), not lower	1610	1780
Porosity (%), not higher	25	21
Ultimate Compressive Strength (N/mm^2), not lower	12.5	28.3
Apparent density (10^3 kg/m^3), not lower	1.80	2.51

Table 9

Properties of Concrete as Compared with specification 14-8-184-75

Characteristics	Value	
	Specification	Concrete developed
Chemical analysis (%)		
SiO_2, not lower	95	96
$Na_2O + K_2O$, not higher	1.2	1.1
Fire resistance (^0C), not lower	1690	1785
Porosity (%), not higher	19	17
Ultimate Compressive Strength (N/mm^2), not lower	15	27.6
Apparent density (10^3 kg/m^3), not lower	2.14	2.40

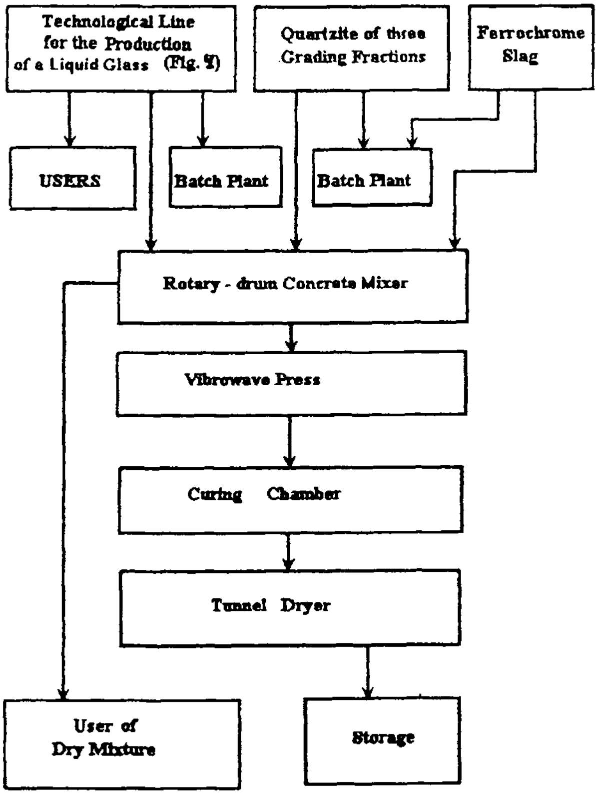

Figure 9. Schematic diagram of the production of Quartzite fireproof blocks at the Department of the West - Siberian Steelworks

4. CONCLUSIONS

1. The mixture proportions and the technology of the concrete developed helps towards the solving of the several problems: environmental (reduction of CO_2 emissions), economic (the cost of the concrete developed is 2 to 3 times lower than that of the conventional one) and social (increase in the house building).

2. The production of unburnt environmentally friendly fireproof concretes from industrial wastes solves the problem of the transportation of refractories - they are not produced in Siberia, makes it possible to use them in the construction of unique objects and buildings with high fire resistance.

3. The work is being carried out as part of the Federal "INTEGRATION" programme (direction № 1, 6).

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Use of crushed waste aggregates for DBM road bases

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The increasing difficulties encountered in retrieving aggregates have stressed the need to find resources which might be alternative to the natural ones. At the same time, the significant increase of debris volume produced by the demolition of civil works has caused great problems in waste storage. A possible recycling use of demolition waste material is its transformation into aggregates to be employed in casting of mixtures. Some recycling experiences have explored the possible use, in concrete casting, of aggregates obtained through the crushing of demolitions. The present work studies the problem of the use of recycled aggregates in casting of bituminous mixtures.

The research has undertaken the characterisation of recycled aggregates in order to verify the limitations of the technical codes in terms of physical and mechanical requirements. Successively, a study to evaluate the affinity of the bitumen and the workability of the mixture, used as a base layer and prepared with recycled aggregates, has been undertaken. The study has been performed by means of the gyroscopic press in order to determine the volumetric characteristics in accordance to SHRP (Strategic Higway Research Program) guidelines.For the best mixture obtained, a performance characterisation has been executed by determining the value of complex modulus as a function of temperature and frequency. The experimental tests have allowed a comparison of the performances between bituminous mixtures prepared with recycled aggregates and those prepared with natural aggregates.

1. INTRODUCTION

The increasing attention towards environmental problems has augmented the difficulties in retrieving aggregates coming from extraction quarries, and, in addition, has made the laws relative to waste material management increasingly strict.

Therefore, the research interest towards new types of aggregates, obtained from the crushing of debris material coming from demolition of structures or constructive components of various kinds, has gained increasing importance.

A material called waste aggregate is obtained from mills which are capable of discarding the undesired content of debris, such as steel reinforcement, wood, plastics, glasses, and so on. Two types of waste aggregates exist, termed 'debris' and 'concrete'. The former is an aggregate obtained from the crushing of brickworks, ceramics, tiles, etc., whereas the latter, more valuable, is obtained from the crushing of plain and reinforced concrete, coming from the demolition of structures or constructive components, such as curbs, 'New Jersey' barriers, piles for electrical air lines, etc. The distinction in the above two categories is performed when waste material reaches the mill. This is an additional requirement of the plant, that is, its capacity of monitoring the incoming material so as to direct it to the store supplying either 'debris' or 'concrete' production. However, it should be noted that a small percentage of brickworks (as small as about 10%) is in any case directed to 'concrete' aggregate type.

The goal of the present research is to evaluate the possibility of employing waste aggregates in the preparation of bituminous mixtures with specific characteristics suitable for their use in road bases of flexible pavements. This is because such a mixture, although it must offer high mechanical performance, does not require specific roughness, abrasion and frost resistant characteristics, which the recycled material could not meet.

In Italy, the use on a large scale of waste aggregates is made possible thanks to the 1996 'Ronchi' law, which has officially recognized the possibility of exploiting the so-called 'marginal' materials coming from building demolition as an aggregate material.

The physical and chemical characterization of the aggregate has been performed through both tests commonly used for quarry aggregates, specifically-designed tests accounting for the particular features of the material. As a reference for the analysis of the results, the Special Contract Standards supplied by ANAS, which is the government company administrating main roads, has been used. In fact, in Italy this standard is usually taken as a reference guideline.

The possible use on a large scale of the material would produce advantages in terms of environmental protection together with a significant economical advantage.

Table 1
Physical characteristics of waste aggregates

G_p – packing specific gravity	1.449 g/cm^3
G_{ap} – apparent specific gravity	2.499 g/cm^3
G_{ag} – bulk dry specific gravity	2.746 g/cm^3
P – porosity	8.99%
N_v – % voids	42.02%
V_e – voids index	0.72
A_w – water absorption	3.04%
SE – sand equivalent *(with floating fraction)*	67.33
SE – sand equivalent *(without floating fraction)*	52.7
I_f – shape index	22.7%
I_a – flattening index	7.8%

2. PHYSICO-MECHANICAL CHARACTERISATION OF WASTE AGGREGATES

The material used in the present research was supplied by Ecoter, Corbetta (MI). It was produced through a crushing plant specifically designed for the production of waste aggregates. It can be classified in 'concrete' category.

Table 2
Mechanical characteristics of waste aggregates

Grading class	Los Angeles value	Resistance to frost
19/8	28.6%	40.7%
8/4.75	26.1%	51.1%
4.75/2	23.2%	54.2%
Average value	25.97%	48.7%
Grading class	**Weight loss after 1 thermal cycle**	**Los Angeles value after 1 thermal cycle**
19/8	0.22%	31.9 %
8/4.75	0.16%	32.2 %
4.75/2	0.20%	26.2 %
Average value	0.19%	31.1%
Grading class	**Weight loss after 5 thermal cycle**	**Los Angeles value after 5 thermal cycle**
19/8	0.39%	31.9 %
8/4.75	0.32%	33.4 %
4.75/2	0.48%	24.7 %
Average value	0.40%	30.0%

The first stage of the research has been devoted to the study of the physical and mechanical characterization of the material. (Tables 1 and 2) For this purpose, the usual acceptance tests for road aggregates have been used along with a number of tests aiming at evaluating both the natural material and if it is possible to modify its characteristics.

The specific gravity of the waste aggregate is similar to that of the aggregates commonly employed in the preparation of bituminous mixes (Table 3). However, it should be pointed out that this is true, provided that the whole aggregate mass is considered, because owing to the mineralogical heterogeneity the value found corresponds to the specific gravity of the various components on average.

During the test for sand equivalent determination, the presence of a floating fraction has been observed. However, this has not affected the test measurements, since it has been possible to account for the floating material layer. Then, the test has been performed by taking away the floating fraction. This has produced a significant decrease of sand equivalent (Table 1), due to the fact that together with floating fraction also the surrounding fine fraction has been taken away. Through spectrographic analysis, it was possible to detect that this floating fraction is mainly composed of silica, that organic groups (CH, NH, etc.) are not present. It is likely that the material analysed represented the lightweight aggregate fraction of lightweight concrete. From the grading analysis it appears that floating material was found only in the 0.850/0.425 mm fraction with a weight content equal to 10%, that is, equal to 0.83% of the whole specimen. Therefore, the floating fraction is negligible.

Table 4
Grading analysis

Sieve size	% Passing
16.00	100.00
12.00	97.48
8.00	72.96
4.75	47.09
2.00	29.34
0.850	19.86
0.425	11.43
0.180	5.58
0.075	2.02

2.1. Grading analysis

Table 4 shows the results of grading analysis performed with the material taken directly from the mill. The specimen was obtained according to CNR 93/83 code.

2.2. Determination of organic substance content

The content of organic substances, determined through colorimetric method, appears to be insignificant.

Table 3
Specific gravity of various aggregates types

Type of aggregate	Specific gravity
waste aggregate	2.746
granite	2.52÷2.90
basalt	2.55÷3.15
porphyry	2.18÷2.90
limestone	2.55÷2.85

2.3. Shape of aggregates

Dimensions of aggregates are conventionally defined as follows:

length (L): maximum distance between two parallel planes tangential to the element;

thickness (S): minimum distance between two parallel planes tangential to the element;

width (D): minimum sieve size for which the element can pass.

According to CNR 95/84, it is assumed that the shape of each element is defined by the following ratios:

shape coefficient $c_f = L/D$

flattening coefficient $c_a = D/S$

stretching coefficient $c_l = L/D$

The above code defines also ranges for the coefficients, so as the shape of aggregate is not acceptable when:

$c_f \geq 3$ e/o $c_a \geq 1.58$

For a set of elements the corresponding shape index (I_f) and flattening index (I_a) can be defined according to the non-acceptable element percentage in the aggregates.

The shape index and the flattening index of waste aggregates are reported in Table 1.

2.4. Determination of weight loss due to Los Angeles abrasion test

The 'Los Angeles test' is fundamental for the characterization of aggregates, since it offers more clearly in comparison to other tests an indication of the mechanical resistance of the material. However, in the case of the material under study, due to the significant petrographic heterogeneity the value obtained should be taken as an average value between relatively much lower values (for instance, for the porfhyritic and basalt fraction) and relatively much higher values (for instance, for the brickwork fraction).

As shown by the results obtained (Table 2), a notable difference between the Los Angeles value relative to higher grading and that relative to lower grading can be observed. This is due to concrete granules that break apart. These in turn cause an increase of the Los Angeles value. Another lesser influencing cause of the above difference is the brickwork percentage difference between the two classes: in the larger-size fraction a slightly higher quantity of brickwork is recorded which causes a worsening of the Los Angeles value.

2.5. Determination of frost resistance

The resistance of aggregates to frost, that is, was determined according to CNR 80/80, has given the results in Table 2.

2.6. Susceptibility to heating

The necessity of verifying resistance to heating, although no guidelines require it, comes from the observation that aggregates, in order to be mixed with bitumen, must be heated at a temperature of about 160-180 °C. This could be dangerous, since the original material was not designed for a use at such temperatures.

In order to verify resistance to heating, it was thought to measure the weight loss due to Los Angeles abrasion prior to and after a thermal shock procedure.

It was decided to use a cyclic thermal action to simulate the worst-case+conditions with more than one heating of the bituminous mix.

In addition to the difference between Los Angeles values it was decided to measure the percentage weight loss, due to organic substances.

Two specimens were prepared according to the specifications of the Los Angeles abrasion test: one was subjected to a single cycle and the other to five cycles. Given the similarity in the results obtained, it was decided not to continue with tests consisting of higher numbers of cycles.

A thermal cycle is composed by four phases. In the first phase of 2 hours, the material is heated from room temperature to 220 °C. In the second phase, the specimen's temperature is maintained at 220 °C for three hours. In the third phase, the specimen is brought from a temperature of 220 °C to room temperature for three hours. Finally, during the fourth phase the specimen's temperature is maintained at room temperature for four hours.

A slight worsening in the Los Angeles value can be noted for each test. Moreover, it can be remarked that the variation is roughly similar for both the tests: this indicates that the material is not susceptible to repeated heating. The slight weight loss is attributed to the evaporation of the water located in the deepest voids. This evaporation cannot be attained by the standard heating at 105 °C.

In the light of the tests performed and of the results obtained, it has been possible to give a first general indication of the physical and mechanical characteristics of the material analyzed.

It should be remarked that the results must be read bearing in mind the material nature, that is an aggregate composed by concrete granules, aggregates for concrete and by a percentage in weight of brickworks (rigorously maintained within 10-15%). This highlights the fact that each characteristic value is actually an average value over those of the various components.

In order to better understand the results obtained from the performed tests, the Special Contractor Standards of ANAS for road bases have been considered. This is because road base has the loosest restrictions among the bituminous layer types. Clearly positive results were obtained for: real volumetric mass, in line with the results for the aggregates commonly employed in bituminous mix preparation; sand equivalent, which is sufficient to ensure a good cohesion between bitumen and fine material; weight loss due to the Los Angeles abrasion test, which is only slightly higher than the limit prescribed by ANAS (by 1%).

Porosity, although it is not mentioned in ANAS Standard for road bases, exhibits a significantly high value, equal to 8.99%, in comparison to the maximum value of 1.5%. prescribed by ANAS for aggregates of base course. This is due to the highly porous fraction of concrete paste. The fraction of brickwork is so small that it cannot influence the overall porosity significantly. The other fractions, consisting of standard aggregates, do not exhibit the above problem of high porosity.

High porosity can directly influence other material characteristics, such as absorption and frost resistance. As a matter of fact, the former approximately double maximum tolerance for a base course, and the latter is fairly higher, Table 1. However, in Italy the value of frost resistance can be considered acceptable because the road bases are rarely subjected to temperatures below 0 °C.

Owing to the above mentioned high absorption, it is strongly recommended that a road base obtained with the above aggregate should be placed on site so as to be insulated from possible water infiltration. From a viewpoint of the use of waste aggregates, given their high porosity, it is likely that in the preparation of bituminous mixes the amount of bitumen to be employed should be higher that that commonly used for traditional aggregates.

3. BITUMINOUS MIXES WITH WASTE AGGREGATES

Similarly to the above aggregate characterization, ANAS guidelines for road bases have been considered in mixture preparation.

The aggregate mixture used is composed of waste aggregate for the 0-16 mm fraction and of calcareous aggregate for the remaining fraction. Calcareous aggregate was chosen firstly because its mechanical characteristics are the closest to those of the waste aggregate, so as to avoid the preparation of a too heterogeneous mixture. Secondly, calcareous aggregates are commonly employed in the preparation of road base bituminous mixtures. ANAS envelope was used as reference for the grading curve (Figure 1).

60/70 natural bitumen was used as the binder. It was decided not to use a modified bitumen in order to keep very general conditions, as well as to better evaluate the contribution of waste aggregate in mix performances.

Bituminous mix design with waste aggregates was performed according to Marshall methodology, which, although it is not the most advanced, is still the most commonly used design methodology in the preparation of standard mixtures.

From the results of the tests (Figures 4-6), the optimal mix is that with 5% bitumen, characterized by 16.50 kN stability, 2.62 mm flow, 6.30 kN/mm stiffness.

For the optimal mix, void content was measured according to CNR 39/73. The mean value of void content is equal to 10.791%, that is, it is substantially in agreement with the reference value of 10% found in the literature. In order to verify the possibility of obtaining such a value after placement, i.e. to verify the reliability of the value obtained, measurement of residual void content has been repeated for specimens prepared with gyroscopic press. This is in order to obtain a compaction similar to that obtained with roller during placement stage. Compaction conditions were those indicated by SHRP-SUPERPAVE methodology for a service temperature below 39 °C and an expected traffic volume during service life of pavement equal to $3*10^6$ ESAL (Equivalent Single Axle Load, equal to 84 kN of force). The compaction level corresponding to the beginning of service life was chosen.

The specimens prepared according to the above specifications exhibited a mean value of void content equal to 11.23%, which confirms substantially the value obtained through Marshall compaction.

After optimal mix composition has been defined, the cohesion between bitumen and aggregate, and its stability in presence of water, was investigated. Since the mixture is designed for road bases, water should not be present. In fact, the upper layers and lower foundation should protect it against water infiltration.

However, since waste aggregates are markedly porous and, hence, susceptible to absorption, it is mandatory to understand if water infiltration can be dangerous.

Two different types of tests were considered. One is aimed at determining directly the separation of bitumen because of water, the other is aimed at measuring the loss in Marshall stability owing to a long period of water immersion of specimens.

3.1. Ancona Stripping Test (AST)

This test methodology [8] allows the qualitative study of both separation and decohesion phenomena. These are governed by adhesion and cohesion characteristics of bitumen. In fact, in the case of a prevailing bitumen-aggregate adhesion in comparison to the internal bitumen cohesion stripping occurs. This is characterized by a reduction of bitumen film thickness. On the other hand, in the case of a prevailing internal cohesion in comparison to adhesion, the separation of bitumen film from aggregate occurs.

The test consists in mixing a 10/6.3 mm aggregate class specimen with the strictly required quantity of bitumen. Then, the mix is placed on the bottom of a 5x5 mm sieve and in turn the sieve is place in a beaker containing an amount of distilled water sufficient to cover aggregates. The beaker is finally placed in another glass container with distilled boiling water.

The reason for using two containers, one containing the other, is to avoid boiling of the water where specimen is placed, which could generate a convective motion creating a mechanical action on the bitumen film.

At the end of the tests, i.e. after 30 minutes of boiling, stripped aggregate surface is sight estimated by five operators. In order to quantify abrasion, the quantity of lost bitumen is also evaluated from the difference between the specimen weight at the beginning and at the end of the test.

The results obtained are: abrasion equal to 43% and a zero bitumen loss.

These results are completely acceptable and very similar to those found in the literature for bituminous mixes prepared with natural aggregates.

3.2. Evaluation of the immersion effect in water on the mix properties (CNR 149)

The test is conducted on Marshall specimens, after a 7-day immersion in water at 25 °C, stability and heaving. Stability is then compared with that of other specimens without previous immersion in water.

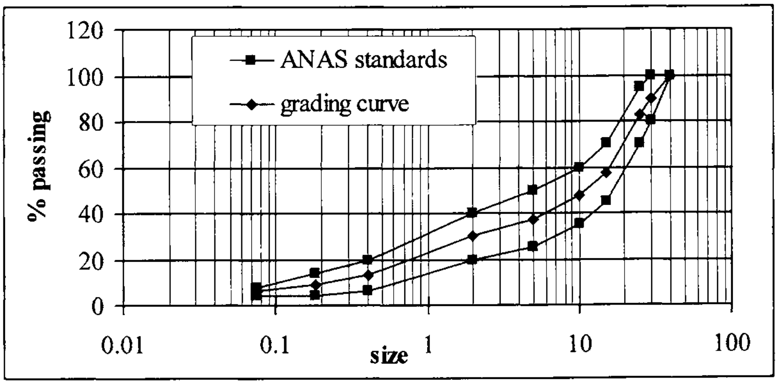

Figure 1
ANAS Standards and grading curve of DBM with waste aggregates

The ANAS Contractor Special Standard describes the present test but with a 15-day immersion period. Therefore, it was decided to consider this period to follow Standards as a reference.

The test gave the following values:

stability loss percentage: 26.67%
volume variation percentage: 1.49%

Volume variation percentage is due to absorption of water during immersion, and, hence it gives an indication of susceptibility of the mix to water absorption in the presence of humidity. The specimens tested showed low absorption despite the high value of absorption exhibited by waste aggregate. This demonstrates that bitumen behaves as a waterproof protective film, which is stable during the 15 days of the test.

The percentage variation of stability value gives a direct indication of the degrading action of water with respect to mechanical performances of mix. If water was capable of provoking the separation of bitumen film from aggregate, a dramatic decrease in the stability value of specimens would occur. In the tests, a decrease of stability equal to 26.67% was measured, which is slightly higher than the maximum value equal to 25% prescribed by ANAS for wear and base courses. However, for these courses much higher performances are required in comparison to those for road bases. Therefore, it can be stated that the decrease of stability caused by immersion in water is not of concern at all.

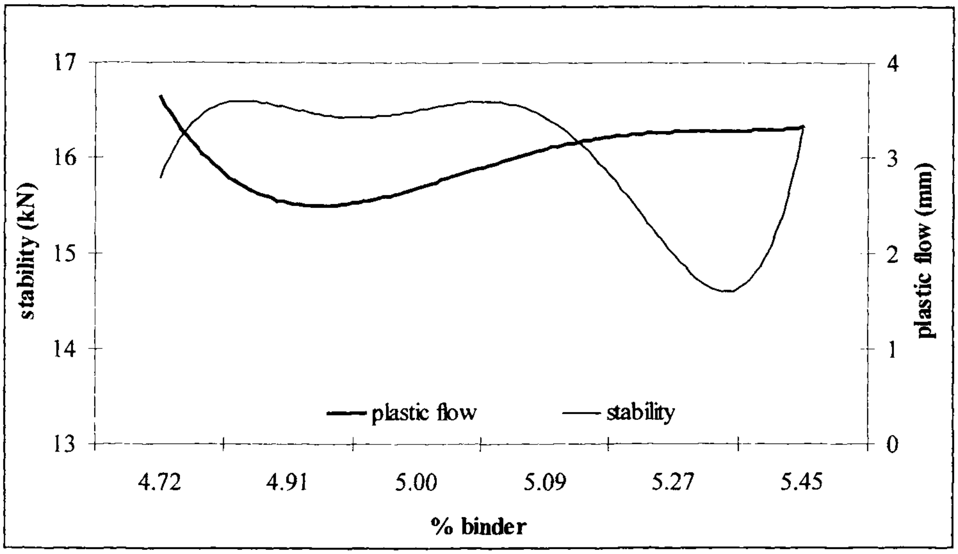

Figure 2
Marshall stability and Marshall flow

4. PERFORMANCE CHARACTERISTICS OF WASTE AGGREGATE BITUMINOUS MIXES

In the last phase of the research, the performance characteristics of the bituminous mix have been compared by taking as a reference, a bituminous mix, also designed with Marshall method and prepared with 60/70 natural bitumen and calcareous aggregates has been taken as a reference. For each of the two mixtures, master curves of complex modulus and phase angle have been obtained according to the methodology proposed by Franken and Vanelstraate. (Figures 3 and 4)

In determining complex modulus and phase angle, load frequencies of 1, 4, 10 and 16 Hz at temperatures of 10, 25 and 40 °C were considered. In comparison to the ASTM D3497-79 guidelines, a frequency of 10 Hz has also been used, since it is characteristic of high speed roads. Moreover, instead of the temperature of 5 °C, that of 10 °C has been considered, since it represents the minimum mean winter temperature for road bases in the north of Italy.

By comparing the master curves obtained, insignificant differences in the behaviour of the two mixtures occur; that is, the differences are similar to those that would be expected if the mixtures were prepared with two different types of calcareous aggregates.

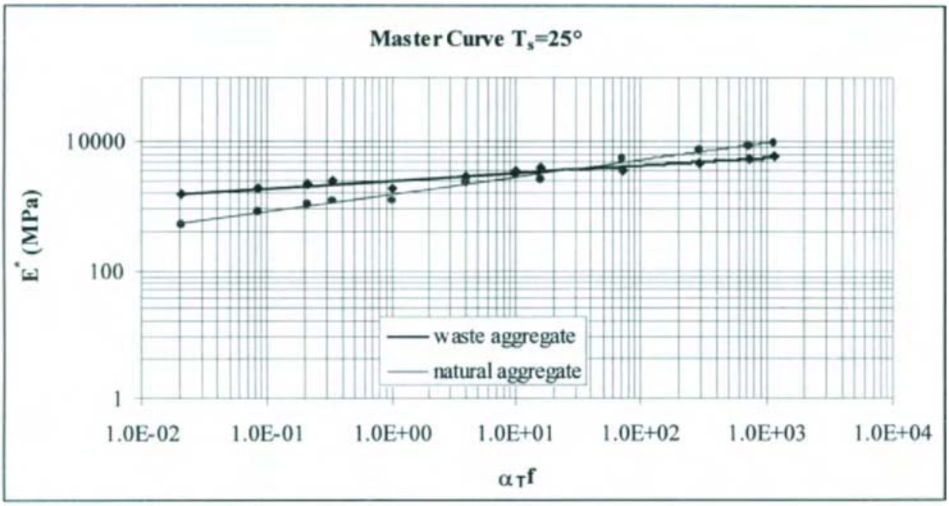

Figure 3
Master curve of complex modulus

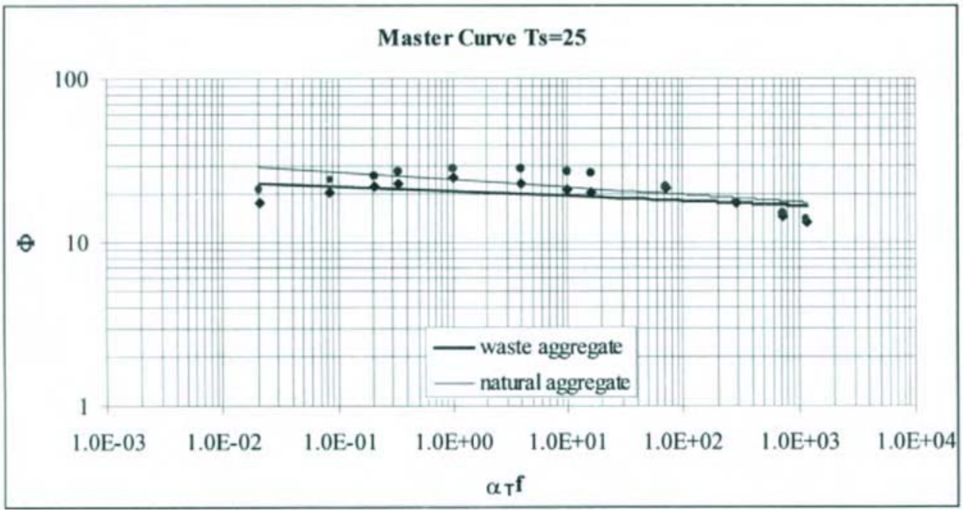

Figure 4
Master Curve of phase angle

5. CONCLUSIONS

The research was aimed at verifying the suitability of waste aggregates obtained from the crushing of debris coming from the demolition of brickwork and concrete structures. The work can essentially be divided in two parts: physico-mechanical characterization of aggregate; mix design along with a verification of the mix mechanical and performance characteristics.

Waste aggregate has been investigated through both common tests for road aggregate acceptance and tests usually employed for concrete aggregates. This is in order to obtain a more complete knowledge of the physical and mechanical characteristics of the material. In particular, a test for evaluating the influence of heating has been conducted; that is, the capacity of waste aggregate of not undergoing modifications of its characteristics due to temperature increases has been assessed. The aim is to verify that the preparation process of bituminous mix does not produce substantial modifications of the material. The results obtained from the first series of tests, compared to with the characteristics required by the Italian organization in charge of the administration of main roads (ANAS), given the assumption of employing waste aggregates in the preparation of road base bituminous mixes, are overall positive apart from porosity. This in fact exhibits a high value due to the presence of concrete granules. The high porosity makes the material susceptible to absorption and, hence, to frost. However, presuming that its use will be for road bases of pavements, that is, under condition of insulation from water, porosity does not represent a too important drawback in the use of the material.

The bituminous mix was designed according to the Marshall methodology, since it is likely to be the methodology mostly exploited in the case of large-scale use of waste aggregates. The optimal mix appears to be that with 5% by weight of bitumen with respect to aggregate. This percentage is slightly higher than that indicated by the ANAS Standard (which ranges from 3.5 to 4.5%), due to porosity of aggregates which causes a high absorption of bitumen. Standard acceptance tests were performed on the mixtures. The results are largely within the code limitations. In particular, recalling the susceptibility to water of the aggregates, the quality of aggregate-bitumen adhesion under humid conditions has been investigated. The results are again within the code limitations.

Since the road base mixtures are characterized by large dimension grading, the suitability of Marshall compaction has been assessed, given its small effectiveness in these cases. Therefore, it was conceived to undertake a comparison with the compaction through gyroscopic press. The results show a coincidence in terms of residual void percentage between Marshall and gyroscopic compaction relatively to a medium design traffic. This infers that, for an expected traffic volume characterized by a medium value, preparation of specimens through Marshall compaction is appropriate.

Finally, performance characteristics (complex modulus and phase angle) of mixtures prepared according to the same protocol and with the same bitumen but with either waste aggregate or natural calcareous aggregate have been compared. (Note that the type of natural aggregate considered is that with the closest physico-mechanical characteristics to those of waste aggregate.) The results are again positive, since from the comparison of master curves (representing the material behaviour at various temperatures and loading conditions) of the two mixtures no significant differences are observed. Therefore, a different behaviour between the mixture prepared with natural aggregate and that prepared with waste aggregate is not expectable.

In conclusion of the present experimental investigation, it can be stated that the examined waste aggregates are perfectly suitable for their use in road base bituminous mixes of flexible pavements.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

The Recycled Materials Resource Center: a new partnership promoting the wise use of recycled materials in the highway environment

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The Recycled Materials Resource Center (RMRC) was formed in late 1998 as a partnership with the Federal Highway Administration (FHWA) to help reduce barriers to the use of recycled materials in the highway environment. The Center has large research and outreach components to its mission. Ongoing research activities are introduced and outreach activities of interest to a European audience are summarized. The Center will be working diligently over the next five years to develop specifications and evaluation methods, transfer appropriate technology, and make information available to the highway community.

1. INTRODUCTION

The Recycled Materials Resource Center (RMRC) is a new national center created to promote the appropriate use of recycled materials in the highway environment. Recycled materials are generally defined as recycled bituminous and concrete pavement materials as well as secondary, byproduct, and waste materials. Situated within the Environmental Research Group at the University of New Hampshire (UNH); the RMRC will soon be moving to a new Environmental Technology Building in the Entrepreneurial Campus at UNH. The Center was formally established on September 4, 1998 in close partnership with the Federal Highway Administration (FHWA) and in coordination with the FHWA Pavement Management Coordination Group. The Center was created through authorization in section 5117(b)(8) of the Transportation Equity Act for the 2lst Century (TEA-21). The RMRC is initially funded for a period of six years.

The Center has a unique role in the growing field of recycled materials use in highway construction --- to serve as a catalyst to reduce barriers to the appropriate use of recycled materials in the highway environment. The Center is a culmination of a number of diverse, but integrated efforts by FHWA, other federal and state agencies, and academia to provide a cohesive approach to the complex engineering and environmental issues surrounding the use of recycled materials. The Center not only will serve as a principal evaluator of information for the FHWA in this area, but also will focus on outreach activities and provide a main point of contact for information.

The Center is staffed with a Director, Associate Director, Outreach Program Project Director, Information Technologist, Program Assistant, research faculty, and graduate and undergraduate students. An Advisory Board comprising state and national experts with interests in recycling issues has been established, which provides guidance and connections to many highway constituencies. The Center has prepared a strategic plan, annual work plans, a practices and procedures manual, self-evaluation plans, performance measure plans, and cost sharing and financial plans to assist in operations.

As stipulated in TEA-21 and in the cooperative agreement between FHWA and UNH, the mission of the Center involves:

> (i) systematically testing, evaluating, and developing appropriate guidelines,(ii) making information available to its clients,(iii) encouraging the increased use of recycled materials by analyzing potential long-term considerations that affect performance,(iv) working cooperatively with Federal and State officials to reduce the institutional barriers and ensure sustained environmental and physical integrity.

In order to fulfil this mission, the Center has identified the following seven principal areas of focus:

> (i) testing and evaluation guidelines and specifications,(ii) material specific research and development,(iii) economics and institutional issues of secondary materials,(iv) new materials and innovative technologies,(v) field trials of secondary materials,(vi) technical services,(vii) technology transfer and training.

The RMRC is concentrating on both research and outreach activities to help accomplish its mission, with State Departments of Transportation (State DOTs) and State Environmental Regulatory Agencies (State EPAs) being the Center==s principal clients. Ongoing research and outreach activities at the RMRC are discussed in the following sections.

2. RESEARCH

Approximately 30 research projects will be conducted by the Center over the six years of operation. The majority of these will be awarded through a national request for proposal and peer review process. From the eleven research projects identified for the first two years, four will be conducted internally by Center personnel, while the remaining eight will be undertaken externally by sub-contractors. Scheduled to commence between October and

December 1999, a summary of a number of these research projects is given in the following sections. Further updates about their progress will appear on the Center==s web site (details given below).

Project 1: Mitigating Alkali Silicate Reaction in Recycled Concrete. This project, conducted by Dr. David Gress of UNH, will take place during years 1-3. Its focus is on the production of concrete containing recycled concrete aggregate (RCA), where the recycled concrete is suffering from alkali silica reaction (ASR). The project succeeds previous work undertaken at UNH to develop test methods capable of identifying the occurrence of ASR . The current project will look at ASR mitigation strategies to control and/or eliminate ASR in concrete containing RCA. A new test procedure for evaluating the use of RCA in concrete with and without mitigation will be proposed to the Association of State Highway and Transportation Officials (AASHTO) for their consideration as a recognized test method. Guidelines will also be developed to allow DOTs to evaluate a given RCA for recycling in concrete. Numerous State DOTs and industrial partners are involved in this project.

Project 3: Environmental Weathering of Granular Waste Materials: Impact on Environmental Performance. Dr. Kevin Gardner of UNH will conduct this project during years 1-3. Work will involve the environmental evaluation of a variety of granular wastes from high temperature industrial processes and will allow an understanding of the geochemical aging and weathering characteristics of these materials. Chemical and physical changes will be assessed using a variety of techniques to enable the prediction of the long-term environmental performance of these materials when used in the highway environment. The project will develop techniques to accelerate the weathering of the material to produce a more physically and chemically stable product. State EPAs and industrial partners are involved in this project.

Project 11: Leaching from Granular Materials Used in Highway Construction during Intermittent Wetting. Dr. David Kosson of Vanderbilt University will conduct this research during years 1-3. The goal of this project is to develop testing and interpretation protocols to estimate constituent leaching from granular waste materials that are utilized as aggregate in unbound highway construction applications (embankments, sound barriers, fill, base course). The resulting test methods and interpretation protocols developed, including appropriate mathematical models, will then be used to evaluate environmental impacts of specific proposed secondary material utilization applications. The primary focus of this work will be on leaching conditions that occur as a consequence of intermittent infiltration (wetting and drying, CO_2 uptake, O_2 uptake) into the granular material. Motivation for end-users to adopt the protocols will be based on the need to evaluate potential environmental impacts for both liability and regulatory assessment. State DOT, State EPAs and industrial partners are involved in this project.

Project 13: Development and Preparation of Specifications for Recycled Materials in Transportation Applications. Dr. Warren Chesner of Chesner Engineering, Inc. will conduct this project during year one. It will address the need for appropriate specifications for using recycled material in the highway construction environment. Fourteen State DOTs from around the nation have agreed to participate to develop common specifications for a number of types of secondary materials within these States. The final output will be the submittal of draft specifications to AASHTO for consideration as formal specifications.

Project 15: Determination of N_{design} for CIR Mixture Design Using the SGC. Dr. Stephen Cross of the University of Kansas will conduct this research project during year one. Work will be carried out to determine the number of compaction revolutions (N_{design}) required in the SHRP gyratory compactor (SGC) in order to duplicate field unit weights of cold in-place recycled (CIR) asphalt mixtures. This work will result in the development of compaction protocol for CIR materials and should remove the final barrier to the further adaptation of CIR technology. State DOTs and industrial partners are involved.

Project 16: Monitoring of a Township Road Constructed with Recycled Tires. Dr. Andrew Heydinger of the University of Toledo will conduct this project during years 1 and 2. It will monitor a township road constructed with recycled tires for climatic effects and pavement deformations. The intention of this work is to determine if there are any early indications of adverse or beneficial effects from using scrap tires in basecourse. Various aspects of the project will include pavement design, pavement construction, and pavement performance. Preliminary guidelines and specifications for constructing asphalt concrete pavements with tire shreds will be drafted and cost-benefits strategies will be evaluated. Ohio DOT and a solid waste district are involved.

Project 17: Development of a Rational and Practical Mix Design System for Full Depth Reclamation (FDR). Dr. Rajib B. Mallick of Worcester Polytechnic Institute in collaboration with members of the National Center for Asphalt Technology (NCAT) at Auburn University for will conduct this project during years 1 and 2. It aims to develop a rational and practical mix design system for FDR. Specifically, the objectives are to develop methods for determining curing periods, number of gyrations required in the SGC to produce in-place densities, and to compare the effectiveness of four different types of additives used for FDR at a specific location in the state of Maine. The resulting mix design system should be able to produce mixes with consistently good performance, thereby enhancing confidence in the use of FDR and encouraging the increased use of recycled materials. Maine DOT is also a principal investigator with the project.

Project 18: Fatigue Durability of Stabilized Recycled Aggregate Base Course Containing Fly Ash and Waste-Plastic Strip Reinforcement. Dr. Khaled Sobhan of New Mexico State University is conducting this research project during year one. The project will evaluate the technical performance of a new composite base course made from crushed RCA, Portland cement, high volumes of coal fly ash, and strips of shredded reclaimed plastics. The primary motivation of this project will be to identify an innovative reuse for recyclable materials in highway pavements by conducting systematic characterization studies aimed at providing valuable insights into the long-term performance and durability issues of such composites. State DOTs and industrial partners are involved in this project.

Project 19: Light Weight Synthetic Aggregate From Fly Ash and Waste Plastics. Mohsen Kashi of GEI Consultants, Winchester, Massachusetts will conduct this project , in collaboration with colleagues from the University of Massachusetts at Lowell and Tufts University during year 1. It will develop a new product from two materials currently sent to the disposal facilities; namely fly ash and waste plastic. The final product, a light weight synthetic aggregate, will be a granular material to be used in such applications as light weight fill, precast concrete elements, concrete structures and insulation for utility pipelines. This project will consider the use of various fly ash to plastic ratios, plastics of different thermal properties and various production methods. The project includes State DOTs and industrial partners.

3. OUTREACH

There are number of outreach activities that have taken place during the first year of the Center or are planned for the near future. Those activities of pertinence to an overseas audience are highlighted in the following sections.

RMRC Web Site: One of the principal information and outreach mechanisms for the Center is its web site http://www.rmrc.unh.edu), which was launched on February 15, 1999. This key component of the Center==s mission is intended to keep the highway community up to date about (i) developments in the field of recycled materials use, (ii) resources, and (iii) Center activities. It features links to international, federal, state, association, corporate, and university web sites as well as links to state specification web pages. The Center==s research projects are featured and will be updated as progress is made. The site also contains a link to the FHWA==s AAUser Guidelines for Waste and By-Product Materials in Highway Construction.@@ In order to make information available to those who would benefit, the site also features a registration form to become a client of the Center and a form to request information.

FHWA International Scanning Program: In September, 1999, the RMRC participated with an FHWA delegation that visited Sweden, Denmark, Germany, the Netherlands and France. The purpose was to review and document innovative policies, programs and techniques in Europe that would help to reduce barriers to recycled material use in the U.S. The delegation met with over 100 representatives from Transportation and Environmental Ministries, research organizations, contractors, and material producers involved with recycled materials in the five countries visited. The delegation was assembled under the FHWA==s International Technology Scanning Program and was sponsored by FHWA, AASHTO (through the National Cooperative Highway Research Program (NCHRP)), and the RMRC. A summary report has been issued to FHWA, a final report is being drafted, and a broad implementation program for the U.S. delegation on significant findings and recommendations is underway. The final report as well as a Power Point presentation about the trip will be made available on the RMRC web page.

Virtual Demonstration Sites: A virtual demonstration site has been established on the RMRC web site where viewers can visit recycled materials demonstration projects and look at photographs, video clips, report summaries, important summary data of laboratory and field testing, together with lists of contacts, sponsors and related publications. This feature will grow over time so that many recycled materials and highway applications will be featured. It should help State DOT and State EPA personnel to visit demonstration sites and >>kick the tires== right from their offices. The Center will be soliciting for additional demonstration sites to add to the database.

Quarterly Electronic Newsletter: The RMRC will develop a concise and informative electronic newsletter to be distributed to all clients who have registered with the Center and to all hyper links associated with the Center==s web page. The newsletter will update research, outreach and training activities coordinated by the Center. By registering with the Center==s web page, individuals will automatically receive the quarterly newsletter.

National/International Conference: The Center will be co-sponsoring a national/international conference in 2001. The likely venue is in the United States. This conference will focus on specifications, accelerated testing, new applications, recycled materials beneficiation, performance modeling, prediction and evaluation, and specific recycled materials and their applications.

4. SUMMARY

Over the next few years, the RMRC expects to make significant advances in the area of recycled materials use in the highway environment. The Center has a broad constituency and will be reaching out to its clients via specifications development, R&D, technology transfer, outreach (web site, newsletters, conferences, training), and information transfer.

Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

CHARACTERIZATION OF LAGOON SEDIMENTS AND THEIR POLLUTANT CHARGE. PROPOSALS FOR REUSING

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The production of dredged mud constitutes a problem of first magnitude for two reasons: the huge amount of generated wastes, and the environmental risk as a consequence of the accumulated and persistent pollutants. Dredging is a routine maintenance activity in many industrial harbors. However, the management of dredging wastes also appears in other circumstances. The Albufera lagoon in Valencia (Spain) is located in a Ramsar wetland. This lagoon has received, over many decades, the pollutants of domestic and industrial activities from the surrounding metropolitan area. In the last century, an increase in the sedimentary process produced an acceleration of filling, decreasing the capacity of the basin. The area is being protected because of its high ecological value.. The aim or the study is to characterize and to quantify the accumulated pollution and compare several alternatives for the use of those sedimentary materials. Heavy metals, organochlorine pesticides, PCB's and Polycyclic Aromatic Hydrocarbons have been identified. The availability of such prime materials for cement production, as material for agricultural soil restoration, and as material for civil engineering construction will be evaluated. Chemical analysis data, that evaluate the degree of persistent pollution, permits one to be optimistic in the reuse of those wastes.

1. INTRODUCTION: DREDGING GENERATES A HUGE AMOUNT OF RESIDUAL MATERIALS

Dredging is an activity that usually produces large amounts of waste materials. For a long time the materials produced by the dredging activities have been used to increase the extension of cultivated lands as well as to produce soils for urban or industrial uses, above all in the nearby areas of the coastal zones and wetlands. Nowadays some activities generate large quantities of dredging materials such as are the maintenance of accessibility of traffic in navigation ways These materials usually accumulate large persistent pollutant concentrations, specially in the surroundings of large industrial ports (Stern & 1998; Jones, 1998; Salomons. S. 1987). Large quantities of mineral residues are also produced in the dredging from lagoons or artificial dams, and in particular those where capacity is regained so that they may be refilled as a result of erosion and runoff..

The Albufera is a coastal lagoon in the center of a wet zone protected as a "Natural Park" near Valencia City, in Spain. The park, is included in the wetlands Ramsar list and constitutes an important ecological enclave in which nest a large quantity of birds and it also serves as a stopping zone for great number as migrant kinds that reach the Europe North. The filling by sediments of that lagoon has not been evaluated accurately, but results show that throughout the last decades the quantity and quality of sediments reaching the lagoon endanger its existence in medium term. On the other hand there is evidence (Peris Mora, & col. 1994) about the quality of pollutants from the metropolitan area surrounding the park. The pesticides used widely in the intensive agriculture area, have produced an accumulation of a whole collection of persistent pollutants.

Through research agreed and financed by the Consellería of Medio Ambiente (Environment Ministry in the autonomous Government) with the Civil Engineering Department of the Polytechnic University of Valencia, a characterization study on the materials of the recent filling has been completed evaluating its pollutant charges and proposing different alternatives for use to simplify the management of the materials dredged.

2. BATHIMETRIC STUDY AND SAMPLE SELECTION

A bathimetríc study using a GPS-Differential system has been undertaken that has produced a new bathimetric map. The sedimentary material contributions have converted the water body into a very shallow lagoon, one which the "iso-level curves" are draw each decimeter (Fig.1). The points for taking samples for different studies have been identified by the same topographic procedure and labeled with a buoy anchored on the bottom. The maximum depth of the lagoon does not reach two meters in any of the points of the lake, which gives the idea of the almost two-dimensional character of the system.

To identify the pollution distribution, in the first series of samples a simple metacrilate corer was used and, after freezing, they were separated into the different levels identified by texture. In the subsequent sampling the use of an average-sample over 1 m was used in the upper sediments. It was thought that this represented a better way to characterize the materials available in a possible industrial dredging operation.

Figure 1: Bathimetric map. Level lines each 10 cm; maximum depth 160 cm

3. EVALUATION OF THE POLLUTION LEVELS IN THE SEDIMENTS

The samples were analyzed for its different parameters to evaluate the possible applicability of various alternatives of use, in addition to toxic characterization and evaluation of the persistent pollutant accumulation. A total of 23 sampling points separating the different sub-levels were used. Thereinafter the decision was taken to select representative samples of the recent sedimentation using an instrument (especially built and patented by us) that permits samples to be taken 1 meter thick. This instrument was used at 23 points in the first stage, and thereinafter accomplished a "denser sampling" on the most contaminated zones at a total of 98 points.

A) Heavy Metals. They were analyzed using ICP-MS lyophilized samples and digested with nitric concentrated acid in a Teflon reactor in microwave oven. This analysis provide information on a great number of elements. The results show local areas where heavy metals concentration was high (zone NW and NE). In these areas the lines of iso-concentration show a high presence of Cr (Fig. 2). In other zones the pollution by heavy metals does show excessive in comparison with studies carried out in the region(CEDEX. 1999). The zone of high accumulation was near the old irrigation channels used in the past as an industrial drain.

Fig. 2 Iso-Concentration lines in ppm of Chromium. Sample-poiunt 4A more than 700 ppm Chromium

B) Chlorinated pesticides were present. The zone was of a high agricultural activity density with intense productivity and more than three annual crops. The presence of pesticides forbidden same time ago were found in meaningful concentrations. For example 12,84 ppb of ppDDT near one of its metabolites the pp'DDD, present in 27 ppb. The highest pollution point contained a total of 43,75 ppb between the seven chlorinated pesticides analyzed.

C) The presence of PCB's analyzed in the seven congeners as per IUPAC is traditionally used as indicative of contamination. The maximum value obtained was 0.86 ppb. This value is very inferior to the maximum tolerated by Spanish management norm of dredgable materials (CEDEX, 93; Oslo Com. 93) that establishes 30 ppb as the limit concentration demanding special management treatment for dredged material.

D) The Polycyclic Aromatic Hydrocarbons were also analyzed (17 congeners) and the concentrations were lower (total maximum from 1,96 ppm) than antropic comparable coastal region sediments (Kennnish, 1998).

E) The analysis of toxicity of the samples used Microtox (EPA) on wet samples. Positive results were obtained in several sediments analyzed. The interference of the ammonia in this analysis necessitates more the research on toxicity on these samples after drying and aeration.

4. STUDIES OF APPLICABILITY

A) *Use as a raw material in cement production:* The cement factories are large consumers of materials. Clay, lime and different composition sands are consumed annually in cement manufacture of various types. The usefulness of these materials as substitute for some of the raw materials presently used in cement manufacture has been tested. The analytical data shows a great uniformity between the different sampling points of the lagoon, and good prospects for possible raw material. The chemical composition and minerals contained in the waste dredged material offers a possible alternative raw material to that of extracted minerals. Other properties of the sediments, solid matter contents or amorfous character of some minerals permits us to consider to these materials with optimism

B) *Use as a raw material in the ceramics industry:* The Valencia Community is a great exporter of ceramic materials to everywhere in the world and in its production consumes large quantities of clay materials. The chemical and mineral analysis offers minimal prospects because large percentages of carbonates limit the massive use of these muds. Nevertheless, a series of experiments have been developed to evaluate the applicability of lower quality ceramic materials such as brick manufacture. The pastes have been analyzed for their possible use as raw material and submitted to chemical and mineral analysis ceramic test and Attenberg index to evaluate plasticity. With the exception of some samples, it could be used as bulk in reduced clay proportions. The excessive percentage of carbonates produced results, though with possible limitations , wich may show a possible outlet for large volumes of material, which is the principle objective of our study

C) *Application in agricultural soil amendments:* Erosion and the subsequent runoff are the process which produce the filling of the dams. With runoff, the finest fractions of soil which contains the most important edafic properties, are lost. Amendments to the soils could consume large quantities of materials originating from dredging. On the other hand it seems that reinstatement of the fine fraction in eroded soils is the most rational and direct destination of these mobile materials. The eutrophic nature of the lake during the years has produced the accumulation of high contents of organic matter that increases the value of that material as agricultural supplement. Studies have been completed but the results obtained to date are promising.

D) *Uses in Civil Engineering ("Friend technology" or "Soft construction"):* The need to find and outlet for dredged materials, that, in the future will be produced in large quantities, suggests that one of the most suitable destinations would be application in infrastructure civil works, where large volumes of materials are used. First study stage has been limited to evaluate the applicability of the materials in works infrastructure within its own Natural Park ("Friend Technology" or "Integrated or Soft Construction"). Since the studies have been directed to establish the techniques and construction in which dredged materials can be used for bicycle-roads or agricultural roads (not for heavy traffic density) in the natural environment. Tests have also been completed for the use of stabilization of the mud with the minimal quantities of binding materials (cement). The work will result in a draft "Manual of Good Practice" in the utilization of the mud as material for infrastructure construction in the natural park. Other applications in public works are the use of dredged materials for restoration of the adjacent beach. It is considered that the beach adjacent to the land that separates the lagoon from the sea and is receding as a consequence, among other causes, of the activities of a great industrial port that interrupts the current of sediments deposit but does not prevent the marine erosion. The direct reinstatement of the sand would demand treatment of dried and granulometric classification of the dredgable sediments to ensure that they are not seriously contaminated, other applications such as the dune area restoration, are being also studied.

5. CONCLUSION

The maintenance of the capacity of the lagoon of The Albufera, a Natural peri-urban park near a population of 1,000,000 of inhabitants, will demand the dredging of contaminated materials from the bottom. The project, accomplished on a small scale so as not to alter the lacustrine ecosystem, will produce in time several million of cubic meters of residual materials. The present study, in addition to evaluating the magnitude of filling up, has analyzed the possibility of valuing those materials through different alternative uses. Table 1, in summarized form, presents some of the more important possible applications.

Table 1 Possible Applications and Review of Properties

Re-utilization Alternatives	Favorable properties	Negative properties	Conclusion
Agricultural soil amendments	Size grain distribution Organic matter Nutrients Water retention capacity Ionic change capacity	Toxic pollutants	Favorable expectations. Application in irrigated land and forest
Cement production	Size grain distribution Chemical composition Partially amorphous character Organic matter Image in the Company Low cost	Chromium excess and other elements Chloride excess Volatile toxic substances Transport cost	Favorable expectations With some caution the mud can be used as raw materials in large quantities
Pottery and tile industry	Plasticity Ceramic properties Mineral composition	Carbonates	Unfavorable expectations The use may be done in brick production, but consumption would be in a small quantity
Civil works "Friendly Construction" or "Soft Technology""	Provision facilities	Expansive clays Too much organic matter	Favorable expectations to be used in a medium/high volume
Dune restoration	Sand size distribution Beaches proximity Soft works compatibility	Clay excess Toxic pollution Organic matter excess	Experimentation pending
In situ immobilization	Non a-biotic character in the bottom of lagoon	Risk on sustainability of same species	The design of dredging techniques in a "Natural Park" to be prudent. Small scale operations must be adopted in all circumstances. In some areas is better to wait.
Controlled dump transport.:	Toxic pollution excess over legal limits	Not accepted by public opinion	In some, limited areas, there is a significant accumulation of pollution. It will be necessary to evacuate in a cleaning process.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

A proposed methodology for in-situ treatment of MSW leachate

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Municipal solid waste (MSW) leachate consists of different constituents (contaminants) having the potential for undergoing chemical, physical and / or biological processes. The normal leachate handling procedure includes collection and off-site treatment, although the concept of landfill bioreactor was recently introduced in which leachate recycling is the main component. The barrier systems which separate the waste from the underlying soil and groundwater, and which minimize the migration of contaminants from the landfill, frequently consist of natural clayey deposits or recompacted clay. There seems to be a tendency towards using active barriers which are capable of removing certain contaminants within MSW leachate, although they are usually designed on a contaminant specific basis. The main objective of this paper is to propose a methodology for the removal of contaminants within MSW leachate, while it passes through different stages each having a certain effect on a single (or a group of) contaminant(s). The mentioned stages can be categorized into three main groups; adsorbant filters (natural and/or natural modified materials and also some type of waste materials), electrokinetic processes and a media for biological growth. However using the proposed systems, may not necessarily result in elimination of leachate collection facilities, but it can have a beneficial effect compared to the treatment methods, also reducing the risk of groundwater contamination.

1. INTRODUCTION

Most of the municipal solid waste (MSW) produced in Tehran is disposed of in non-engineered landfills. The population of Tehran is likely to increase up to 15,000,000 by the year 2021. This means a daily MSW production of about 13,000 tons, on a 0.8 - 1 Kg/cap.day basis. Construction of engineered landfills followed by an appropriate site selection procedure is foreseen in the development programs, which will certainly require a realistic and practically applicable provision for minimizing both the adverse impacts of leachate on the surrounding environment, and the related costs.

It is worth noting that even in engineered landfills, problems may arise, which in turn may reduce the efficiency of leachate handling facilities. The hydraulic conductivity of the barriers is subject to increase as a result of interactions between the leachate and the barrier. Cracks may also occur (due to constructional reasons) causing direct channelling of the leachate and increasing the risk of contamination of the underlying soil and groundwater. In some cases, dual leachate collection systems are of interest, which can substantially increase the related costs.

Offsite treatment also poses some problems depending on the type of the treatment process (e.g. chemical and/or biological). Biological and particulate clogging of the leachate collection pipes is also a problem.

in-situ treatment of the MSW leachate as an alternative to conventional methods, has neither been experienced nor proposed to date, and the authors believe that this can be a basis for further research.

2. GENERAL SCOPE

To assess the need for in-situ treatment of MSW landfill leachate, four main factors should be taken into account; (1) the problems with existing leachate handling procedures, (2) cost of offsite treatment, (3) utilization of some waste materials as part of treatment system and (4) environmental impacts.These are now considered.

Leachate collection systems, have been designed in a similar manner to agricultural drainage systems. This causes problems such as blockage of pipes (both particulate and biological). In addition leachate interaction with clayey barriers can significantly increase their hydraulic conductivity resulting in an under-designed function of collection system.

Lechner (1992) lists the types of damages to the collection pipes which can result mainly from construction loading as well as clogging (both particulate and biological) (Lechner, 1992). Therefore it seems necessary to ensure rapid removal of leachate, and the ability to inspect, maintain and repair the drainage system (Lechner, 1992), which may identify practical difficulties and costly activities.

Clayey barriers, as the most frequent used liners, should clearly have a low hydraulic conductivity (usually 10E-9 m/sec or less), as a basic requirement. The main problems related to utilization of clayey barriers can be categorized as follows:

-their hydraulic conductivity is subject to increase as mentioned earlier

-cracks may occur due to local settlements causing direct channelling of leachate

-even if leachate mounding does not occur, there will still be diffusion of contaminants (Mc Dougall et al., 1995), (Rowe, 1992).

Collected leachate is treated mainly by evaporation ponds, recycling and/or biological treatment systems. However,evaporation ponds can be of little applicability in wet climates and they may also have an adverse impact on public health where used.

Leachate recycling as the basic requirement for landfill bioreactors, having its own technical difficulties, seems to be a reasonable practice to enhance the biological activities within landfills (Reinhart et al., 1998). In other words, different methods of leachate recirculation may have disadvantages such as; being incompatible with closure, potential subsidence impact on trench integrity and being inappropriate for use in inclement weather (Reinhart et al., 1998).

Biological treatment systems, have been experienced mostly in the form of anaerobic-aerobic process combinations, which in turn can increase the costs and the requirements for proper control, although still efficient in reduction of environmental contamination.

3. LEACHATE COMPOSITION

MSW produced in Tehran is mainly composed of about 70% food wastes, 10% plastics, 10% paper and cardboard and 10% of other types of waste. The high content of food wastes, together with high moisture content of about 75%, are the factors positively influencing the biodegradability of the waste introduced to the landfill sites. Little data is available about the quality of leachate produced as a result of biological process at the sites receiving Tehran's MSW, but a Biochemical Oxygen Demand (BOD5) and Chemical Oxygen Demand (COD) of about 16,000 mg/lit and 27,000 mg/lit respectively, a Total Suspended Solids (TSS) of about 73,000 mg/lit and a total nitrogen of nearly 1000 mg/lit, were reported once by the Organization of Material Reuse for Kahrizak landfill (south of Tehran) leachate. These values can be used in preliminary investigations, although the age of landfill and other related factors have not been specified. Leachates found elsewhere may have nearly the same characteristics (e.g. Keele Valley in Canada (Rowe et al., 1997) and the United States (Reinhart et al., 1998)).

Heavy metals can be found in MSW leachate originating from unengineered disposal of items containing metals, like dry-cell batteries (Ni, Cd and Hg) and car components such as Pb-acid batteries (Alshawabkeh et al., 1995).Heavy metals have not been measured within the leachate solution found at landfill sites of Tehran, but due to the different types of wastes being disposed of in such sites, significant concentrations are likely to be found in the leachate.

Consideration of the typical values of biodegradable fraction (BF) for different types of wastes (about 0.80 for food wastes, 0.50 for paper and cardboard) and the high content of the food wastes, paper and cardboard in Tehran's MSW, leads us to the conclusion that the leachate is highly biodegradable and capable of being treated under anaerobic conditions if provided. Even a contaminant like Dichloromethane (DCM) which is a volatile liquid and which readily diffuses through high density polyethelene (HDPE) geomembranes (Rowe et al., 1997), has been shown to be biodegraded as it migrates through both intact and compacted clay (Rowe et al., 1997).

4. MATERIALS AND METHODS

Four main groups of activities are proposed for the in-situ treatment process; (1) TSS reduction, (2) capture and/or extraction of heavy metals, (3) sorption of some non-biodegradable organic compounds and (4) biological reduction of biodegradable fraction of the leachate. Each of the above mentioned groups of constituents (contaminants), can be treated by certain processes and methods.

Suspended solids should be removed at earlier stages so as to prevent particulate clogging of drainage pipes.

Heavy metals can either undergo sorption or extraction mainly by electrokinetic processes. A series of leachate-clay interaction experiments, performed by Dearlove (1995), indicates that cations such as K, Na, and Mg appear to be sorbed onto the surface of boulder clay, while Fe and Mn show significant concentrations associated with the colloidal phase in the leachate, either bound to organic colloids or forming separate inorganic colloids.

Electrokinetic process is also considered as a promising technology for in-situ treatment of soil contaminated with inorganic and organic contaminants. The related processes (electro-osmosis, electro-phoresis and electrolytic migration of ionic and polar species) are well discussed by Pamukcu et al. (1995) and Alshawabkeh (1995).

It is important to note that different types of soils (particularly clay) have different sorption characteristics. The relationship between the type of clay mineral and the selectivity sequence is shown in Table 1 (Alshawabkeh et al., 1995).

Table 1
Selectivity order for some clay minerals

Adsorbent	Selectivity order
Montmorillonite(Na)	Ca>Pb>Cu>Mg>Cd>Zn>Ni
Illite	Pb>Cu>Zn>Ca>Cd>Mg
Kaolinite	Pb>Ca>Cu>Mg>Zn>Cd
Smectite, Vermiculite	Zn>Cd>Mn>Hg

The surface charge density of the clay mineral, characteristics and concentration of cationic species, existence of organic matter in the soil and PH are the factors affecting the adsorption/desorption mechanism (Alshawabkeh et al., 1995).

A series of laboratory experiments conducted by Pamukcu et al. (1995), provides strong evidence that heavy metals such as Cr, Cs, Sr and U can be removed by electrokinetic processes as a method for controlling their migration from landfill sites. Average percent reduction of the mentioned species are shown in Figure 1.

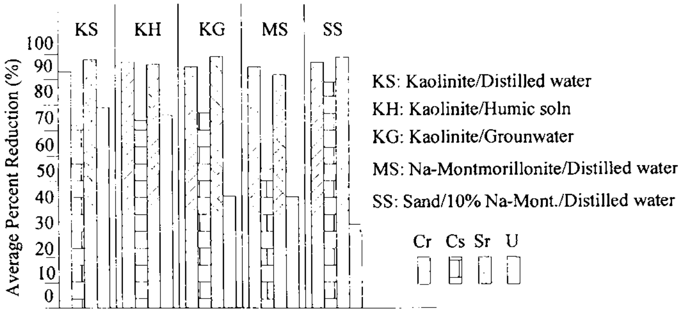

Figure 1. The efficiency of heavy metal removal by electrokinetic process (Pamukcu, 1995).

Organic compounds such as Methylene Chloride (MC), Trichloroethylene (TCE), Toluene, m-Xylene and others are often found at landfill leachate. Park et al. (1995) showed that tyre chips had 2.5 to 10 percent of the sorption capacity of Granular Activated Carbon (GAC) on the volume basis, in a series of batch sorption tests with the organic species including MC, TCE, Toluene and m-Xylene. Based on the study mentioned, they propose the use of tyre chips instead of granular materials in leachate collection systems because of the advantages it gives, including; decreasing persistent organic compound concentration in liquid phase, giving a longer detention time for biodegradation, providing ideal sites for microbial consortia to grow and maintaining constant liquid phase concentration by sorption/desorption.

The effects of organoclays on sorption of hydrophobic organic chemicals have also been experienced by Nzengung et al. (1997). Organoclays which can be produced by replacement of exchangable inorganic cations with quaternary alkylammonium cations, have an increased interlamellar spacing, and consequently a high sorption capacity, so that they have been proposed as components of landfill clay liners because of acting both as sealants and as effective sorbents of dissolved organic contaminants (Nzengung et al., 1997).

Anaerobic environment at the bottom of landfills, in the form of a medium consisting of natural and other types of materials, provides the appropriate condition for the biodegradable portion of the leachate to be degraded. The impact of controlling factors including; moisture content, PH, temperature, availability of macro- and micro-nutrients and suitable micro-organisms on the landfill stabilization, have been widely studied to date (Reinhart et al., 1998). Another important parameter is the detention time of the leachate within the anaerobic medium. This can typically be selected nearly equal to the value considered in offsite treatment systems, although some modifications might be necessary. This implies that leachate may have to be kept within the system for a predetermined period of time, in other words, leachate can be drained out discontinuously.

The thickness of the anaerobic layer can be calculated based on the required detention time. For example if a layer with an hydraulic conductivity of 10E-5 m/sec is to be used and a detention time of 10 hours is to be achieved, Darcy's equation can be used as a preliminary estimation.This result in a thickness of approximately 55 cm if a maximum of 30 cm leachate mounding is assumed to occur above this layer. It is worth noting that the changes in hydraulic conductivity resulting from biofilm growth and particulate clogging should not be ignored.

An effective technique for accelerating the biological degradation of organic matter, is leachate recirculation (Reinhart et al., 1998). This has shown quite satisfactory results related to removal of Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) at different landfill sites.

Complementary nutrients and micro-organisms of interest can also be introduced to the system and may include raw domestic wastewater or sludge.

5. THE PROPOSED SCHEME

An in-situ leachate treatment system is proposed consisting of different layers each designed to remove certain species of contaminants. Table 2 summerizes the specifications required for each layer.

Some of the waste materials can also be used as bottom liners or landfill caps reducing the volume of waste to be disposed of and the related costs and even being effective in removal of certain contaminants. Examples of such materials are:

-Demolition wastes with low hydraulic conductivity, and sufficient durability and strength, serving as landfill lining material (EL-Sohby et al., 1995).

-Industrial by-products such as Pulverised Fuel-Ash and Papermill sludge, with low permeability and plasticity, as landfill caps (Sarsby et al., 1995).

-Fly-Ash Composite (a mixture of Fly-Ashes, soluble silicates and/or lime) with the possibility of grass growing suitable as landfill caps. Its hydraulic conductivity is shown to decrease and the unconfined compressive strength is stated to increase with time, making this composite a proper lining material (Quant, 1995).

- Rubber-Kaolinite and Rubber-Bentonite liners which minimize cracking, are readily available,are easy to handle and compact as liner systems (Baykal et al., 1995).

Table 2

Proposed layers for in-situ treatment of leachate

Layer number	Materials	Contaminants to be removed	Additional processes
1 (top)	Sandy clay clays, ...	Heavy metals	Electrokinetic processes
2	Organoclays, shredded tyres, ...	Non-biodegradable organic compounds	Addition of organic cosolvents (if necessary)
3 (bottom)	Sand, Gravel (sufficient clay content)	Biodegradable organic compounds	Nutrient addition, PH adjustment, seeding, leachate recirculation

The proposed system is schematically shown in Figure 2.

6. CONCLUSION

Different constituents found in MSW landfill leachate can be removed by different processes such as electrokinetic process, sorption and biodegradation.

Based on the literature reviewed to the extent available, various materials and methods have been introduced separately to overcome the existing problems of leachate handling. Combining the results of such investigations, leads us to a different conceptual approach about waste materials and landfills. Landfills can be considered as effective solids waste treatment systems not simply as a place to dump the solid waste.

The proposed in-situ treatment system has now to be studied in detail through extensive laboratory and field investigations.

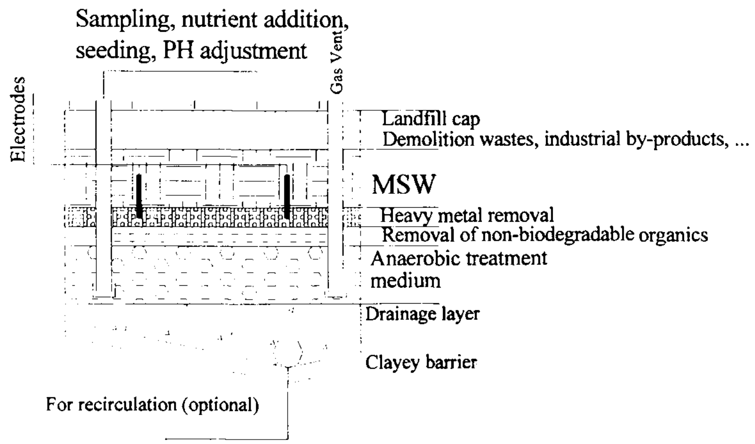

Figure 2. The scheme of the proposed in-situ leachate treatment system.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Re-use of arisings and waste materials for reinstatements

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The use of secondary aggregates and industrial by-products to modify arisings or excavated materials from reinstatements is discussed in this paper. Laboratory testing and field trials are required to develop mix compositions with the best engineering properties and long-term performance.

1. INTRODUCTION

Since the introduction of the New Roads and Street Works Act 1991 (NRSWA) and the publication of the statutory Code of Practice 'Specification for the Reinstatement of Openings in Highways' (Department of Transport et al, 1992), hereinafter referred to as the NRSWA Specification, considerable change has occurred in the way highway openings and reinstatements are carried out. The NRSWA Specification, which provides guidance on materials and compaction methods for openings in the highway, is currently under review to update and clarify a number of elements including the use of secondary and recycled materials. It is likely to allow more freedom for utilities to use recycled materials.

The introduction of the Landfill Tax in October 1996 and the proposed tax on natural aggregates are being used to encourage waste producing industries to adopt a re-use policy. Moreover, the supply of materials from traditional aggregate sources is likely to become increasingly constrained. These changes will, over time, encourage more use of waste, secondary materials and industrial by-products in construction.

Increasing environmental and commercial pressures, within the Utility Industry, to reduce operational costs associated with trench reinstatements have encouraged a specific focus on the potential re-use of arisings (excavated material) from trenches in the highway. These actions complement the Government's drive and initiatives towards sustainable development and waste minimisation in construction.

Extensive road trials have been undertaken to develop a design guide and specification for cold in-situ recycling of highway pavements (Milton and Earland, 1999). It provides the latest best practice advice on the design and supervision necessary to reconstruct the foundations and/or structural layers of road pavements. An earlier report by Potter (1996) embraced the principles of waste minimisation and best value in road haunch construction. The design guidance addressed reusable materials, including alternative materials and recycling, together with details of layer thickness for equivalent performance.

Knowledge of this research and associated publications is aiding highway authorities and utilities, through the Highway Authorities and Utilities Committee (HAUC), to encourage and promote the use of recycled materials for trench reinstatements.

2. UK STRATEGY FOR SUSTAINABLE DEVELOPMENT

In 1992, about 180 countries met at the 'Earth Summit' in Rio de Janeiro to discuss how to achieve sustainable development. A plan of action, Agenda 21, was agreed which recommended that all countries should produce national sustainable development strategies. The UK was no exception and produced their strategy in early 1994. Following on from this, a consultation document, 'Opportunities for Change', and a summary leaflet for the public were published. (Department of the Environment, Transport and the Regions, 1998). The integrated approach to sustainable development and the inclusion of a social dimension were widely welcomed. It proposes international co-operation as a key to sustainable development and company environmental and sustainable development reporting as ways of achieving the objectives. Because sustainable development objectives are broad, one way to deliver them is through the use of indicators. About 150 indicators have been set up to allow tracking of the objectives and to identify priorities for action. One of these actions is to tackle the 145 million tonnes of waste arisings generated per annum. Targets are being set towards waste minimisation, re-use, recycling and recovery. Of the waste annually generated from commerce, industry and households, only 31 per cent is currently recycled and 63 per cent is sent to landfill (1997 estimate).

2.1. Minerals guidance

The Department of the Environment Minerals Planning Guidance (MPG6) document (Department of the Environment, 1994) provides advice to mineral planning authorities and the minerals industry. Information is given on the ways in which the construction industry should receive an adequate and steady supply of material at the best balance of social, environmental and economic cost, whilst ensuring that extraction and development are consistent with the principles of sustainable development.

Four main objectives are set out, of which the first two are directly relevant to the re-use of excavated materials. These are:

- to conserve minerals as far as possible, whilst ensuring an adequate supply to meet the needs of society; and
- to minimise production of waste and to encourage efficient use of materials including appropriate use of high quality materials and recycling wastes.

MPG6 stresses the need to use all aggregates efficiently by minimising waste and avoiding the use of a higher-grade material if lower grade sources are fit for the purpose. It suggests that, whilst specifications for the use of material must have an adequate margin for appropriate performance, over-specification tends to occur and materials are used with performance characteristics higher than required for the purpose. One of the main reasons for this is the relatively low cost of primary aggregates from naturally occurring quarry sources in the UK.

In general, the regulations are designed to encourage the use of waste, secondary materials and industrial by-products. The majority of the materials that are available from excavations are relatively inert and therefore applicable to the needs of the utilities industry when re-use of excavated material is required. However, in the case of materials that are unsuitable for re-use, the utilities would bear the cost of disposal.

Utility companies and contractors can minimise the use of primary aggregates by following the waste hierarchy rules:

1. Reduce the quantity of materials used.
2. Re-use excavated materials at the work site.
3. Recycle previously excavated material stockpiled off site, possibly treating unsuitable materials to render them usable.
4. Dispose of unwanted arisings.

If the materials are unsuitable for immediate re-use, they can be removed to a depot and processed to render them fit for re-use. However, this may be difficult because the materials are often a mixture of different types of soils and granular materials that require separation in order to form a material either directly suitable as backfill or suitable once treated.

3. SECONDARY MATERIALS

Secondary materials may be used, either directly or after processing, in the reinstatement of openings in the highway if it can be demonstrated that they are suitable for this purpose. These may include:

Reclaimed bituminous material
Building demolition materials
Slate quarry residues
Minestone spoil
Crushed concrete
China clay sand
Spent oil shale

The use of industrial by-products to improve the engineering quality of excavated materials may include:

Blast furnace slag
Furnace bottom ash
Pulverised fuel ash
Rubber crumb
Unburnt colliery spoil
Steel slag
Burnt colliery spoil
Sewage sludge incinerator ash.

The availability of many of the industrial by-products and secondary aggregates are very localised with the result that they are only economic in specific areas. Nevertheless, methods that minimise the work required on site are likely to be the most effective, especially those that minimise problems with compaction (Burtwell and Spong, 1999).

4. NRSWA SPECIFICATION

In order to understand better the process of achieving sustainable development within the utilities industry, consideration needs to be given to the requirements of the New Roads and Street Works Act (NRSWA) 1991. Under Section 71 of the Act, an undertaker executing street works must comply with the materials prescribed in the NRSWA Specification and observe standards of workmanship that will lead to satisfactory compliance.

Provision is made within the NRSWA Specification for the re-use of excavated materials by stabilisation with lime and/or cement to render them fit for use. This technique has been used successfully in the construction industry in large-scale projects and is now of interest to the utilities both on site and at a depot. An important requirement in the Specification is that utilities must meet the performance criteria for reinstatements irrespective of the materials used in the reinstatement. Therefore, whichever material is used in the reinstatement of an opening in the highway, it must produce both short-term and long-term performance that complies with set national standards. It is also required to produce an equivalent performance to materials traditionally used as backfill/sub-bases/roadbases in highway openings.

In order to re-use arisings, it is important to consider the constraints or additional requirements given in Section S5.4 of the NRSWA Specification. These include frost heave susceptibility, maximum particle size and stabilisation. Stabilisation, a process whereby excavated materials may be improved or stabilised by mixing with cement or cement blends, can render them suitable for use at backfill and/or sub-base levels in the reinstatement.

4.1. Backfill material

The backfill material classifications are relevant to materials whether they are imported or derived from on-site excavated materials. The classification of different materials and their use should be in accordance with Appendix A of the NRSWA Specification. The materials are categorised into Classes A to E according to the California Bearing Ratio (CBR) i.e. the load bearing capacity of the material as shown in Table 1.

The materials listed under Class E are similar to those in the Specification for Highway Works (SHW), Clause 601 (Manual of Contract Documents for Highway Works). They should not be used at any level within the permanent structure of any reinstatement and should be sent for disposal.

Table 1

Backfill material classifications and CBR values

Material Type	Backfill Class	Material Performance CBR (Per cent)
Graded granular	A	Over 15
Granular	B	7 to 15
Cohesive/granular	C	4 to 7
Cohesive	D	2 to 4
Unacceptable	E	Less than 2

Source: HAUC Advice Note 4, NG5.1 (Highway Authorities & Utilities Committee, 1996)

5. PROCESSING OF EXCAVATED MATERIALS

The most common method of reinstating the road pavement is by using imported high quality materials such as Granular Sub-Base Type 1 (GSB1). However, in specifying the method of stabilisation, the NRSWA Specification permits the engineering properties of lower quality materials to be improved thus saving primary aggregates. Two methods are considered in this paper. Other methods are likely to be possible whereby one or more by-products are used in conjunction with the basic excavated material.

5.1. Stabilisation

The method of stabilisation should be subject to laboratory testing to establish that a stabilised backfill in material is capable of achieving the assumed limiting performance of any of the backfill materials permitted by Appendix A1 of the NRSWA Specification and Table NG5.1 in Notes for Guidance in Advice Note 4. The resultant stabilised material should then be equivalent to backfill material Class A, B, C or D, depending on the CBR value found in the laboratory testing.

Proprietary stabilisers are available but none have yet been demonstrated to be fully successful in laboratory tests or field trials. Alternatively, additives, secondary materials and by-products can be used e.g. cement, Pulverised Fuel Ash (PFA) and foamed bitumen. For cement and PFA stabilisation, the compressive strength requirements of the NRSWA Specification for Foamed Concrete for Reinstatements (FCRs) could provide the reference criteria. For materials stabilised using foamed bitumen, the Indirect Tensile Stiffness Modulus (ITSM), measured using the Nottingham Asphalt Tester (NAT), could be used as the engineering criterion.

Other alternatives may be possible by using a variety of blends of by-products with different excavated materials. For example, incinerated sewage sludge could be added to Classes C or D materials or reclaimed bituminous-bound paving material for stabilisation with cement, PFA or foamed bitumen.

The main objective of laboratory testing is to determine the mix compositions needed to produce appropriate performance within the reinstatement and surrounding pavement.

5.2. Cement-bound excavated material

The use of foamed concrete formulations are methods of improving excavated materials to make them acceptable for use as backfill in reinstatements, but such methods will need to be subject to further research. The current specification for foamed concrete is considered too restrictive in terms of particle size distribution and clay content. The basic criterion for acceptance for reinstatement should be based primarily on performance. Stabilisation of the excavated materials can be carried out using a cement/water 'grout'. This material does not necessarily need a foaming agent, indeed it is expected that better results could be obtained with a plasticiser. The 'grout' modified material needs to flow, thereby eliminating the need for compaction. Three basic methods can be used to adjust the strength of the material to be stabilised: varying the cement content, varying the water content or varying the density of the material. The requirement is to achieve the target strength in the most economic way.

Laboratory testing and field trials would provide evidence of the engineering properties and the performance of the cement bound excavated material.

None of the main sources of secondary materials, including reclaimed bituminous-bound paving materials, and industrial by-products are thought to adversely effect watercourses or the environment, so they could be used by utilities. Baldwin et al (1997) described a detailed review of the potential of industrial by-products and reclaimed materials to cause contamination of ground or surface water when used in pavement or earthworks construction. The potential impacts of using industrial by-products in conventional engineering situations were found to be within the range permitted by the strictest water quality standards (UK Drinking Water Quality Standards). Hence, these materials could, in most instances, provide an alternative to traditional methods without giving rise to ground and surface water pollution.

6. CONCLUSIONS

The main conclusions are:

1. A pro-active culture of sustainable construction to support the conservation of primary aggregates needs to be encouraged within the utility companies and promoted through each company's environmental policy.
2. The relative merits and economics of the type of plant available for processing excavated materials should be investigated further.
3. The use of secondary aggregates and industrial by-products to modify excavated material for reinstatements is practicable. However, laboratory testing and field trials are required to develop mix compositions with the best engineering properties and long-term performance.

ACKNOWLEDGEMENT

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

Cold in-situ recycling of structural pavement layers

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In-situ recycling of pavement materials has become an increasingly important feature in the UK for the maintenance of highways. The concept of using the existing highway as a "linear quarry" from which roadstone aggregates can be reclaimed has gained favour for both environmental and economic reasons and has been the subject of a three year research programme at the Transport Research Laboratory (TRL). The project, which was sponsored by the Highways Agency, CSS (formerly the County Surveyors Society) and Colas Limited, addressed the use of the technique for the structural maintenance of roads carrying between 2.5 and 20 million standard axles (msa).

1 INTRODUCTION

The concept of the linear quarry provides environmental benefits including a reduction in the extraction of primary aggregates; a reduction of materials disposed off-site; a reduction in the use of energy; a reduction in the amount of construction traffic servicing maintenance sites; and, a reduction in traffic congestion from shorter duration roadworks. Furthermore it promotes sustainable development and improvement of the road network within the guidelines agreed at the 1992 Earth Summit in Rio de Janiero (Agenda for Change, 1993). The general public, central and local government and the transport industry will all benefit from a more widespread use of the processes.

2 DEFINITION

In the context of structural maintenance of highway pavements, the term "cold in-situ recycling" refers to the techniques using specialist plant to pulverise and stabilise existing road materials, in-place, at ambient temperature, with the addition of hydraulic and/or bitumen binders. In the United Kingdom, the bitumen binder used is normally foamed bitumen and the hydraulic binder is generally Portland cement, sometimes used in conjunction with lime or PFA.

3 DEVELOPMENT OF ROAD RECYCLING WITHIN THE UNITED KINGDOM

Today in some European countries recycling is a standard alternative for both construction and maintenance, particularly where there is a shortage of road-building aggregate or no indigenous bitumen. In the UK, however, a plentiful supply of good quality aggregate, relatively short distances between quarry, mixer and site and a wide range of specifications reduced the need and impetus for recycling. This situation is now changing in line with the environmental considerations mentioned above, with changes to the national specifications for road building and maintenance and with large influential road building companies promoting the use of recycled materials.

Although plant and procedures for cold in-situ recycling of structural pavement layers have been used in the UK for some years, there were no nationally consistent guidelines on their use until the publication of TRL Report 386 *Design guide and specification for structural maintenance of highway pavements by cold in-situ recycling* (Milton and Earland, 1999) in October 1999.

The cold, in-situ recycling of structural pavement layers was previously accepted and encouraged for lightly trafficked roads as a valuable alternative to traditional reconstruction. When used by a Local Highway Authority the design was usually based on advice from the specialist contractor and often governed by the practical restraints of the site.

For motorways and trunk roads which are the responsibility of the Highways Agency the process was permitted for pavements with a design traffic level of up to 5 million 8 tonne standard axles (msa). The Specification contained within TRL Report 386 which is now available within the Highways Agency's library of specifications, SPECLIB, enables the technique to be used (subject to specific approval) on schemes, for which they are the overseeing organisation, with design traffic loadings of up to 20 msa.

Part 1 of TRL Report 386, the *Design Guide* contains information and advice relating to environmental considerations and site evaluation, which are necessary for the design of cold in-situ recycled materials and their use for the structural maintenance of highway pavements. The design process includes flow charts and methodologies for layer thickness determination on a graphical basis for use by designers. The many variables associated with recycling existing roads inevitably mean that there are a number of aspects to be carefully considered by the designer. The Guide provides a refined, easy to use structural solution taking into account all of the options available from the initial site investigation, to determine the suitability of the existing materials for re-use, either as reclaimed materials for off-site use or for in-situ recycling, through to the structural design of the finished pavement.

Part 2, the *Specification and Notes for Guidance on the Specification* for cold in-situ recycled material are presented as stand alone sections; the separate specification clauses may be used unchanged or adapted for inclusion within the standard contract documentation for structural maintenance works. Furthermore, the possibility exists within the Specification to adopt non-destructive test methods to establish end-product performance of the in-situ recycled layer. By reference to the associated Notes for Guidance, the designer is able to make reasoned decisions relating to the site-specific items of the specification contained in the respective Specification Appendices.

4 RESEARCH METHODOLOGY

4.1 Introduction

TRL recently completed a three year investigation of cold, in-situ, recycling of structural pavement layers using both cement and foamed bitumen binders (Milton et al, 1999). Data were collected from a review and examination of nine in-service roads which had been maintained, by Local Authorities, using cold in-situ recycling techniques over the preceding decade. In addition, the research included the construction and monitoring of full-scale trials on the A3088, Cartgate Link Road, in Somerset.

4.2 Recycled pavements

The in-service roads had been constructed over a range of subgrades and were designed to carry, over a 20 year period, traffic loadings ranging between 2.5 msa and 20 msa. The Local Authority Engineers were not subject to the current traffic limits permitted in the HA specifications. However, despite the fact that much of the earlier cold in-situ recycling work in the UK was undertaken using cement or lime as the primary binding agent, the search for sites carrying medium to heavy traffic revealed only two cement bound sites designed to carry this level of traffic.

The site of the full-scale construction trials, on the A3088 in Somerset was a 15-year-old, two-lane single carriageway road that was built as a major access route linking the industrial estates and ferry ports to the south to the A303 trunk road to the north. The A3088 was built over much of its length following the near level alignment of an abandoned railtrack, passing through a rural landscape for the most part at grade or on shallow embankment but with short lengths of cutting. The original road had exceeded its design life and distress was present in the form of surface rutting and cracking. Interpretation of deflections from a series of deflectograph surveys showed that the residual life had been exceeded.

The original pavement construction comprised 100mm of asphalt surfacing over 140mm of wet-mix macadam roadbase founded on a Type 1 sub-base of variable thickness of between 150 and 470mm, built to reflect the changes in the CBR of the subgrade.

The Cartgate Road trial was carried out in two phases in consecutive years. Phase 1 of the trial occupied the full-width of the north and south bound lanes over a length of 1.25km, divided into eight trial sections varying in length between 100m and 150m; the monitored length of each bay was standardised at 100m. In addition, there were two control sections constructed using conventional materials, one of flexible design and the other of flexible composite design. Four of the trial sections were constructed using a cement stabilised recycled roadbase and four with foamed bitumen bound recycled roadbase. The sections included not only different binder agents and thickness of treatment, but also different combinations of source aggregate, dependent on how much of the existing pavement was removed prior to pulverisation.

For Phase 2 of the Cartgate Road trial two adjacent full-width, 600m long sections were constructed on a further stretch of the A3088 to test the viability of draft specifications for both cement bound and foamed bitumen bound cold in-situ recycled material under normal contractual conditions. In both sections, the recycled materials comprised aggregates reclaimed from the wet-mix roadbase and sub-base layers of the existing road, which were exclusively constructed using crushed carboniferous limestone from the Mendips.

4.3 Performance assessment

A prime objective of the Linear Quarry project was to assess the performance of road pavements containing cold, in-situ recycled structural course material as a means of validating a structural design method. To achieve this, the performance and condition of each of the nine in-service roads was assessed by measuring the following parameters:-

- Past traffic carried
- Extraction of representative cores
- Visual survey to identify and record surface defects
- Determination of in-situ stiffness modulus from a Falling Weight Deflectometer survey
- Laboratory testing of core specimens:
  - Bulk density by gamma-ray scanner
  - Bulk density by weighing in air and water
  - Indirect tensile stiffness modulus using the Nottingham Asphalt Tester
  - Core compressive strength/estimated cube strength of cement bound material

The data collected from monitoring the in-service roads were supplemented by data collected from the Cartgate Road trials. During construction of these trials quality control and compliance testing of the materials was carried out to determine:-

- Particle (lump) size distribution
- Moisture content
- Cube refusal density
- As placed density determination using a Nuclear Density Meter
- Thickness of recycled layer
- Cube compressive strength of moulded samples
- ITSM of moulded samples (foamed bitumen material only)
- Compositional analysis (foamed bitumen material only)

Following construction of the Cartgate Road trials the performance for each of the test sections was assessed by the following condition indicators for up to 3 years:-

- Visual inspections
- Falling Weight Deflectometer surveys
- Deflectograph surveys (carried out routinely by the Highway Authority)
- Traffic Assessment
- Extraction and laboratory tests on cores
  - Bulk density by gamma-ray scanner
  - Bulk density by weighing in air and water
  - Indirect tensile stiffness modulus using the Nottingham Asphalt Tester
  - Core compressive strength/estimated cube strength of cement bound material

Compilation and subsequent analysis of the data collected as outlined above enabled comparisons to be made between the in-service performance of the sites and their original design.

4.4 Structural design

The relationship between the thickness of the recycled structural course and the traffic loading for the sites where foamed bitumen binder was used is summarised in Figure 1.

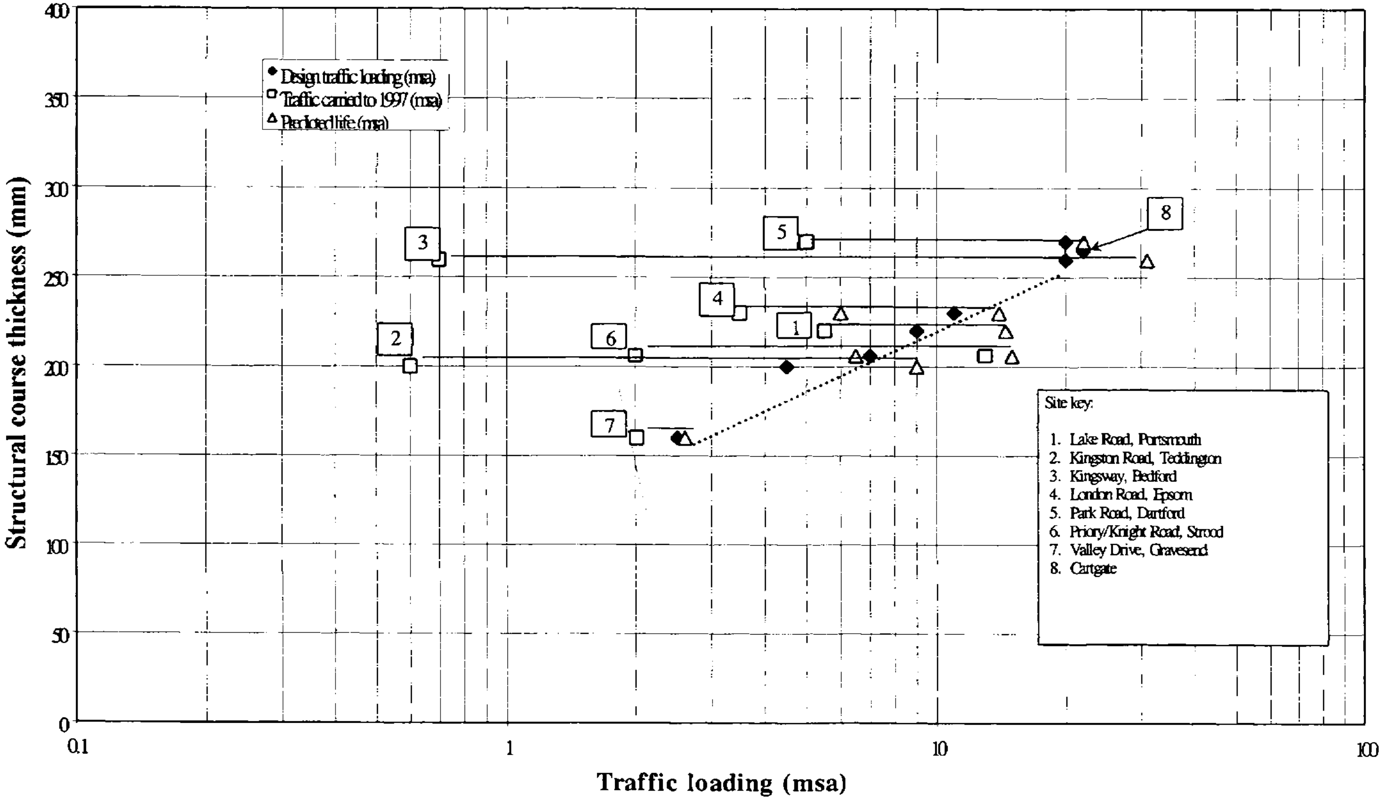

Figure 1 Predicted life in relation to design traffic loading with structural course thickness design line using cold in-situ foamed bitumen bound recycled material

The results of the research carried out for roads recycled with foamed bitumen binder, showed that in all but one site the predicted life of the recycled road, from deflection measurements, was at least as long as the design life. Therefore, the plotted dashed line, in Figure 1, was considered to offer a reasonable design curve for traffic loading between 2.5 msa and 20 msa, associated with a standard foundation, dependent on subgrade conditions and 100mm surfacing comprising standard asphalt materials of 100mm thickness.

Similarly, a consideration of the findings from roads recycled with cement enabled a design curve for these materials to be formulated. As was the case for the foamed bitumen bound design, for traffic loadings between 2.5 msa and 20 msa the design curve assumes a standard foundation dependent on subgrade condition and has associated with it a variable thickness of hot-mix asphalt surfacing.

5 SPECIFICATION

The initial aim of the research was to draft a specification moving away from recipe and method requirements towards those of end-product performance, measured in-situ by non-destructive tests or by laboratory tests on core specimens extracted from the finished pavement. However, to assure the durability of the material produced by the cold in-situ recycling techniques, it was found necessary to retain some detailed recipe specification clauses.

6 CONCLUSIONS

The research carried out at TRL has shown that the structural maintenance of road pavements by cold in-situ recycling can be a sustainable and appropriate method of maintaining roads with design traffic loadings up to 20 msa or possibly higher.

The design guide and specification that emanated from the research has been shown to be workable and robust under normal contractual conditions. As the process becomes more widely used and greater volumes of material are recycled, this design guidance may be subject to development in the light of the increased data available.

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Waste Materials in Construction
G.R. Woolley, J.J.J.M. Goumans and P.J. Wainwright (Editors)

A preliminary investigation of the removal of heavy metal species from aqueous media using crushed concrete fines

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The crushing of reclaimed concrete in the production of recycled aggregate produces a large volume of fine material which is rich in hydrated cement paste phases, the coarser fraction being predominantly composed of the primary aggregate. It is the coarse fraction which is of use in construction and the fine fraction which is destined for landfill. The application of ordinary Portland cement (OPC) based materials in the solidification and stabilisation of heavy metal-bearing wastes is well established. Accordingly, it is proposed that this fine, cement-rich fraction of OPC-based waste may be used to immobilise heavy metal species from aqueous media. The removal of heavy metal nitrates (Pb^{2+}, Ba^{2+}, Zn^{2+}, Ni^{2+}, Cr^{3+} and Cu^{2+}) from aqueous solution by the addition of crushed OPC concrete waste (in the particle size range 1 – 2 mm) is reported herein. The extent of exclusion of the metal ions indicates that mechanisms other than pH-dependent precipitation are in operation. The fate of the heavy metal species has been determined by scanning electron microscopy.

1. INTRODUCTION

In an effort to preserve natural resources and reduce the landfill burden, the UK government is encouraging the use of the cement-based component of demolition waste (essentially concrete and mortar) as a source of recycled aggregate for which a target of 55 million tonnes per annum by 2006 has been set [1]. The crushing of reclaimed concrete in the production of recycled aggregate produces a large volume of fine material which is rich in hydrated cement paste phases, the coarser fraction being predominantly composed of the primary aggregate. It is the coarse fraction which is of use in construction and the fine fraction which is destined for landfill.

In the USA, where stringent disposal regulations for heavy metal-bearing waste are in force, OPC is generally used to stabilise and solidify such waste prior to disposal in landfill [2,3]. The primary mechanism of cement-based immobilisation has been identified as the reduction in solubility of heavy metals at elevated pH. It is proposed that the cement-rich, fine fraction of concrete-based demolition waste could reduce the solubility of aqueous heavy metal species by this mechanism. The work described herein was intended to test this postulate.

2. EXPERIMENTAL

The mix composition of the waste concrete investigated in this study is listed in Table 1. A jaw-crusher was used to crush the concrete which was then graded according to particle size. 10 g samples of the 1 - 2 mm concrete fraction were added to 100 cm^3 of individual metal nitrate solutions containing 100, 1000 and 10 000 ppm Pb^{2+}, Ba^{2+}, Zn^{2+}, Ni^{2+}, Cr^{3+} and Cu^{2+}. Similar specimens were set up using 100 cm^3 of mixed metal nitrate solutions containing 100 and 1000 ppm of each metal. The solutions were filtered after 24 hours (at room temperature) and analysed by ICP. The concrete particles were dried in air at 105°C for 12 hours prior to SEM/EDAX analysis and the collection of secondary electron images.

Table 1
Mix design and strength data of waste concrete.

Constituent	Property
Cement	28.32 kg
Water	11.37 kg
5mm aggregate	13.90 kg
10mm aggregate	44.22 kg
20mm aggregate	43.87 kg
100mm cube strength	65 MPa
75*75mm core strength	53 MPa

3. RESULTS AND DISCUSSION

The fine concrete fraction was effective in the removal of heavy metal ions from aqueous solution (Tables 2 and 3). The concentration of each metal ion in individual and mixed-metal solutions after 24 hours was lower than the solubility of the metal hydroxides at the corresponding pH and temperature [2]. This indicates that precipitation mechanisms, in addition to the reduction in solubility at elevated pH, are responsible for the immobilisation of the metal ions. Secondary electron micrographs of the metal precipitates formed on the surface of concrete particles from 10 000 ppm individual metal solutions of (a) Cu^{2+}, (b) Ni^{2+} and (c) Zn^{2+}, are shown in Figure 1. EDAX analysis of the bladed copper-containing crystals indicated a Ca:Cu molar ratio of 1:11. A Ca:Ni molecular ratio of 1.10 was observed for the botryoidal nickel-containing precipitate. The cubic crystals observed on the concrete particles following residence in Zn^{2+} solution were found to be calcium-rich, whereas the underlying precipitate was zinc-rich.

The back-scattered image and X-ray elemental maps for Ca, Si, Pb, Cr, Ni, Cu and Zn, of the surface of a concrete particle after 24 hours exposure to a mixed metal solution (1000 ppm w.r.t. each metal species) are shown in Figure 2. The back scattered image shows a layer of precipitated material of approximate thickness 140 μm on the surface of the particle. The elemental map for Ca illustrates the migration of calcium from the cement phase and its participation in the mixed metal precipitation. Conversely, no migration of silicate species was observed. A relatively high proportion of lead was shown to have precipitated out on the cement matrix rather than in the precipitated layer as was the case for chromium, copper and zinc. It is possible that isomorphic substitution of Ca^{2+} by Pb^{2+} (ionic radii 1.00 and 1.17Å, respectively [4]) has taken place in the cement matrix. Nickel-rich bands of precipitate were observed on the surfaces of the precipitate.

Table 2
Concentration and pH of individual metal solutions after 24 hours in contact with 1-2 mm size fraction of crushed concrete waste.

Initial Concentration (ppm) of metal	Concentration (ppm) and pH after 24 hours											
	Pb^{2+}		Ba^{2+}		Zn^{2+}		Ni^{2+}		Cr^{3+}		Cu^{2+}	
	Conc	pH	Conc.	pH	Conc.	pH	Conc.	pH	Conc.	pH	Conc.	pH
10 000	100	12.3	7000	12.6	4000	6.2	2000	7.6	1000	3.6	2500	4.7
1000	100	12.5	500	12.5	<1	12.2	<1	12.2	50	5.5	<1	12.4
100	-	-	40	12.5	2	12.5	<1	12.5	4	12.4	3	12.4
Initial pH of 10 000 (ppm) solution	3.0		6.6		4.7		4.9		1.9		3.8	

Table 3
Concentration of metals and pH in mixed metal solutions after 24 hours in contact with 1-2 mm size fraction of crushed concrete waste.

Initial Concentration (ppm) of metal	Initial pH	Final pH	Concentration (ppm) and pH after 24 hours Pb^{2+}	Ba^{2+}	Zn^{2+}	Ni^{2+}	Cr^{3+}	Cu^{2+}
1000	2.7	7.8	<1	900	2	50	<1	<1
100	4.4	12.4	<1	50	<1	<1	<1	<1

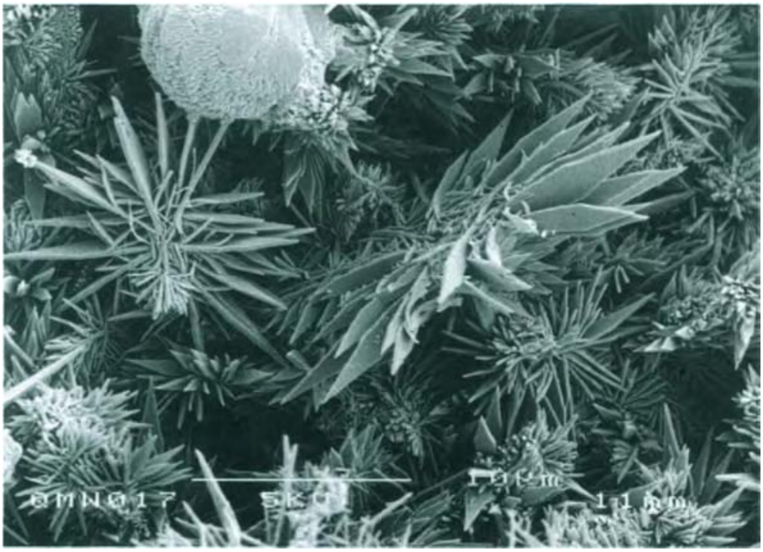

Figure 1a. Spectacular bladed crystals formed from 10 000 ppm copper solution.

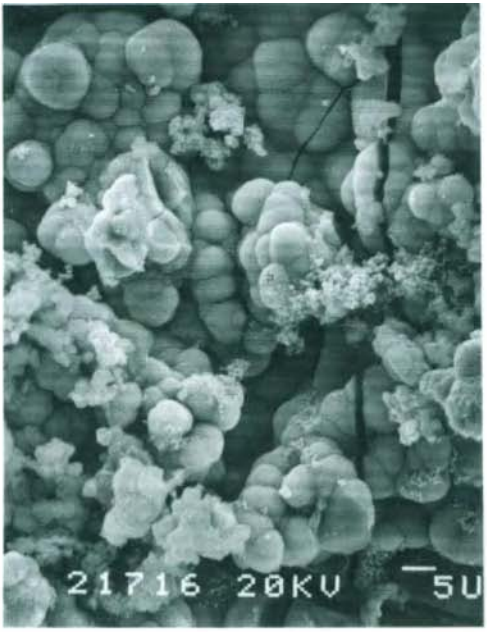

Figure 1b. Botryoidal precipitate from 10 000 ppm nickel solution.

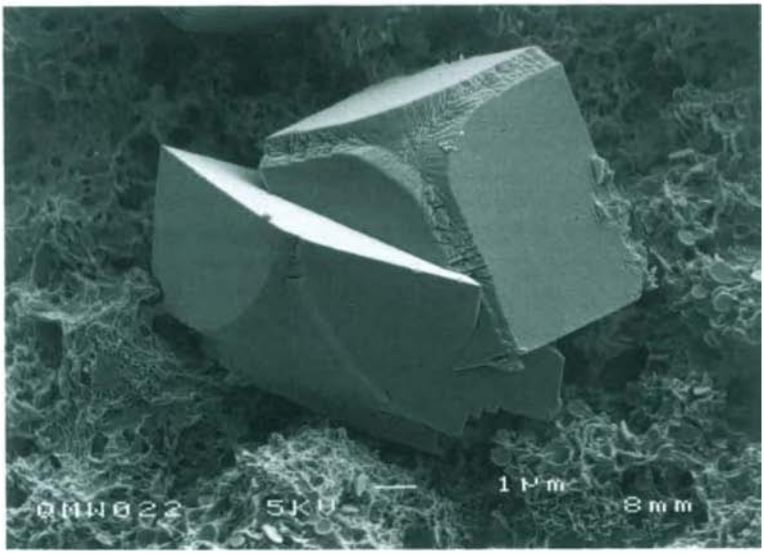

Figure 1c. Cubic and platy morphology of material precipitated from 10 000 ppm zinc solution.

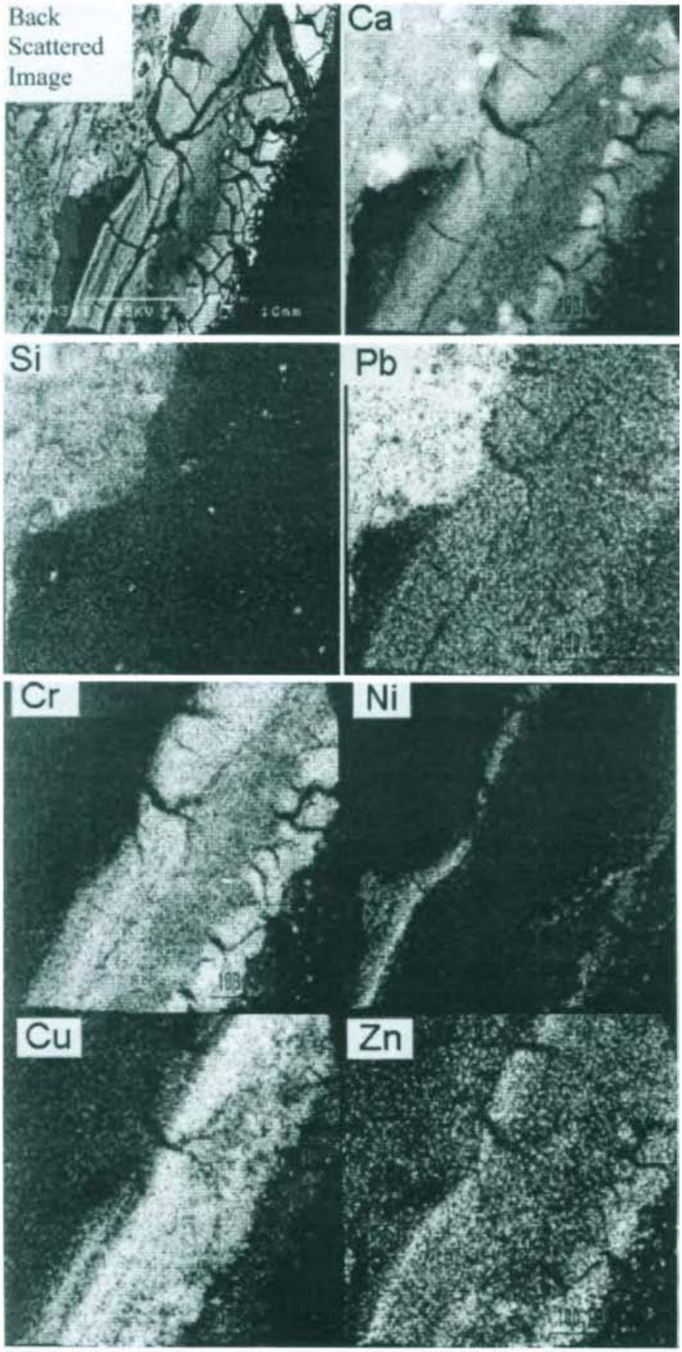

Figure 2. Back scattered electron images and X-ray maps for cement paste particle and surface precipitate from 10 000 ppm mixed metal solution. Width of each image is 250 μm.

4. CONCLUSIONS

This preliminary study has shown that crushed concrete fines are effective in the removal of heavy metals from aqueous solution. The extent of exclusion of the metal ions indicates that mechanisms other than pH-dependent precipitation are in operation. Calcium ions have been shown to migrate from the cement matrix and to participate in the co-precipitation of metal species on the surface of the concrete particles. The removal of Pb^{2+} from solution is, at least in part, believed to be attributable to isomorphic substitution of Ca^{2+} by Pb^{2+} in the cement matrix. Further research is required to examine the efficacy of this method of heavy-metal immobilisation in real waste streams along with a cost-benefit analysis of recovering demolition-waste fines for this purpose.

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