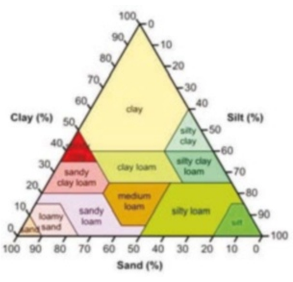
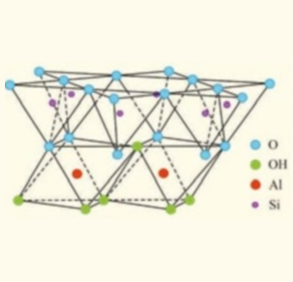
THE SCIENCE OF CLAYS

Applications in Industry, Engineering and Environment

Swapna Mukherjee





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The Science of Clays

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To
my parents

FOREWORD

Lord Byron in one of his poems called the clays "light and worthless". Truth can never be so diametrically opposite. Twenty four by seven we use something routed through clay, from our food to shelter to power to medicine to utensils and to what not! It is so omnipresent that we rarely recognise its actual significance. "The Science of Clays" by Dr (Ms) Swapna Mukherjee is, thus, another eye-opener to the scientific community. The book is an outcome of her life-long association with the Mineral Physics Division of the Geological Survey of India and I feel privileged to compose a few lines on her challenging mission.

The book has been thoughtfully divided into three parts, viz., the basics, the industrial interface and the environmental impact. The first part titled "Understanding the clays: Their formation, constituents and properties" describes their origin and evolution, chemical composition and structure and finally their chemical and physical properties. The second part under the title "Industrial uses of clays and argilloids" deals with the applications in glass, ceramic, refractory, cement, medicine, electrical and mining industries as also in agriculture. The third part, "Clays in the environment", illustrates the two poles – the beneficial and hazardous consequences.

The basic properties actually determine their industrial use for a particular purpose and hence they are analysed in depth *vis a vis* their applications. Variation in quality and quantity in the natural source and even their modifications are discussed. Materials which have clay-like properties are also included. Clays are known to buffer many hazards but at the same time their fine particles cause both air and water pollution. The author presents an unbiased balanced view on the environment.

By and large, the book is a commendable systematic scientific document and a must reading material for all subject matter specialists dealing with clays in any manner whatsoever.

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PREFACE

The comprehensive scientific study of any object involves obtaining the basic idea about it, its socio-economic applications, and its environmental impacts, if any. An integrated study of clays that unifies these three widely separated aspects – viz., the science of clays (that involves the understanding of their origin, composition, internal structure, physical and chemical properties etc.); the industrial uses of clays; and the applications of clays in environmental protection – are therefore essential for laying the foundation of academic researches, industrial developments and environmental sustainability. Besides, further research and development on the industrial and environmental applications of clays necessitate an understanding on the relation between the attributes (composition, internal structure, physical and chemical properties) of clay and its usability for a specific purpose. For example, zeolites in clays are used as drilling mud for their tunnel type of crystal structure that enables absorption of some typical fluids and their extrication on heating; kaolinites for their property of hardening on being heated are used for various ceramic productions; the ion-exchange property of clays enable them to be utilized in radioactive waste disposal etc. Few books cover, in a multidisciplinary approach, the comprehensive explanations for the geological, physical, chemical, industrial and environmental aspects of the clays and the interrelationship of these aspects. This book endeavours to provide a complete description of all these widely varying aspects to fill up this hiatus.

The book is divided into three parts. At the beginning of Part I, precise and unambiguous definitions of clays and their constituents are given along with clear and succinct explanations. The subsequent discussions of Part I cover the vast and diverse spheres of the science of clays that include their origin and evolution in nature; their composition and internal structure; their physical and chemical properties; and soil mechanics. The analytical techniques for determination of clay constituents are also described in this part.

Part II describes the application of clays in industry in different forms, with an emphasis on the substitution of metals with clays, e.g. ceramics etc. Exhaustive descriptions are given here for uses of clays and their derivatives in various industries, like the abrasive, insulators, drilling fluids, ceramics (modern and traditional uses), cements, fillers, plasters, surface coatings, fertilizers, batteries, soil conditioners, pigments, medicines and electronic equipments. The relation between the physical and chemical properties of clays and their industrial applications are explained as much as practicable.

Part III comprises a thorough description of the roles of clays in environmental protection and degradation. The environmental impacts of clay mining, beneficiation and clay-related industries; and the natural processes by which clays protect the environment are explained in the initial chapters of Part III. The next chapters introduce the application of clays and their derivatives to resist pollution, recycling of industrial waste products and waste managements (for both toxic and non-toxic wastes).

The information provided in these three parts is expected to provide the readers a comprehensive idea regarding various aspects of clays and an understanding of the relationship between different disciplines of physical, chemical, earth and environmental sciences that covers these aspects. For the students, research scholars and professionals of various branches of technology, earth sciences and environmental sciences, this book aims at giving a clear conception of various branches of clay mineralogy, their interrelations and to provide a more comprehensive knowledge of their own disciplines.

I express my deep appreciation to Shri Bhaskar Ghosh, my collaborator in this book, a researcher in Presidency University, Kolkata and Assistant Professor in Jogamaya Devi College, University of Calcutta, Kolkata. He has written the first chapters of each part of this book (i.e. chapters 1, 7 and 16) giving an overview of the contents of subsequent chapters.

February, 2013 **Swapna Mukherjee**

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This book has resulted from the immense amount of help and encouragement from many of my friends, colleagues and scientists working in related areas. I am particularly indebted to the Geological Survey of India, my colleagues there of different departments and laboratories for providing various kinds of help and suggestions. Thanks to Prof. H.N. Banerjee of the Geology department of Presidency University, Kolkata. My sincere thanks to Prof. Sugata Hazra, Director of School of Oceanography, J.U. and Prof. P. Sengupta, Geology Dept., J.U. I appreciate the interactive help from Mousumi Banerjee, Geolgist of G.S.I. Thanks are particularly due to Miss Dola Chakraborty for the technical help throughout the work.

Interactions from the students, while teaching in different universities, helped me to frame the structure of the course to fulfill their current need in this field. The success of the book will depend on how the students for whom this is written are benefited and how this is received by the teachers who will guide them in this subject.

Last but not the least, this book is the outcome of continuous support, encouragement and help from my husband, Prof. P.K. Mukherjee and daughter, Swagata.

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PART I Clays: Their Formation, Constituents and Properties

PART II Industrial Uses of Clays and Argilloids

PART III Clays in the Environment

PART I

Clays: Their Formation, Constituents and Properties

CHAPTER

1

CLAYS AND THEIR CONSTITUENTS – DEFINITIONS AND A BRIEF OVERVIEW

Clay, a natural mixture that is plastic when wet and hard when dried or fired, is composed largely of clay minerals and some other materials. The clay minerals, which are hydrous silicates containing aluminium, potassium and some other cations, impart in the clay its characteristic properties. The quality of a clay and its industrial uses largely depends on the type and proportion of clay mineral(s) present in it. The clay minerals are very stable in the humid, oxidising environment prevailing at or near the surface of the earth. They are produced in nature mainly by interaction of rocks with water, oxygen etc. through chemical weathering, hydrothermal alteration and other natural processes.

Clay is the object of study of this book. To have a comprehensive idea of any natural abiotic object, we first need to know what it actually is and how does it differ from other objects; so an unambiguous definition of it must be given first. Then we can proceed to study different aspects of that object like its composition, its classification, its physical and chemical properties, its formation and occurrence in nature, and its socio-economic importance (including its uses in industry and environmental protection etc.).

All the above aspects of clay are discussed in this book. The present chapter lays a foundation for this discussion – it presents a comprehensive explanation for the universally accepted definition of clay; describes the constituents of clay, and elucidates their formation in nature. A brief description of important types of clay is given at the end of the chapter.

Contributed by Bhaskar Ghosh, Kolkata, India

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1.1 CLAY: DEFINITION

Since 16th century, clay attracted the interest of scientists and technologists of different disciplines, who gave different definitions for clay to suit their respective needs. By the term *clay,* sedimentologists indicate all the sedimentary particles having grainsize <1/256 mm; mineralogists refer to certain phyllosilicate minerals; and engineers mean a fine grained material having certain mechanical properties. All these ambiguities and confusion necessitated formulation of uniform and universally acceptable definitions for clay and clay-related substances. The Joint Nomenclature Committee (JNC), was constituted from the Association Internationale Pour I'Etud des Argiles (International association for study of clays, AIPEA) and Clay Minerals Society (CMS) to give the following definition of clay in 1995 that may be acceptable to all:

The term "clay" refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired (Guggenheim and Martin, 1995, 1996).

The materials that fulfil all the conditions stated in this definition are kaolin, china clay, bentonite, bleaching earth, common clay, ball clay, fire clay, and refractory clay. The different aspects of the definition are explained below.

- **(a) Naturally occurring material**: To qualify as clay, a material must be naturally occurring. Any synthetic substance cannot be called clay. For example, fly ash can be fine grained, and may show considerable plasticity when wet. But it cannot be termed as clay because it is man-made. Some authors consider *laponite* as clay, but in this book it is not regarded as clay as it is synthetic.
- **(b) Fine-grained:** There is no universally accepted size limit for clay: sedimentologists use <4 μm, soil scientists use <2 μm, and colloid chemists use <1 μm particle size. Guggenheim and Martin (1995) recommended to give the actual dimensions of the particles, e.g., particles less than 4 μm.
- **(c) Minerals:** Clay is composed of minerals. Since minerals are inorganic, a substance composed largely of organic materials cannot be termed as clay. That excludes peat, muck, some soils, etc. that contain large quantities of organic materials.
- **(d) Plastic at appropriate water contents:** Unconsolidated, dry clay particles form a sticky, plastic mass when water is added to it. *Flint clay* and *Fuller's earth* do not have this property. But these two materials have resemblance with the clays regarding their origin, constituents and industrial uses. For this reason, many authors consider them as clays. In this book, the JNC-recommended definition of clay has been strictly followed, and the term *argilloid* (clay-like) is used instead of *clay* for such materials.
- **(e) Harden when dried or fired:** The plastic wet clay hardens upon drying and firing. When air-dried, the material turns to a hard, brittle mass, which

can be brought back to initial state by crushing. But when fired, it turns to a rigid, rock-like mass which cannot be brought back to initial state (Fig. 1.1).

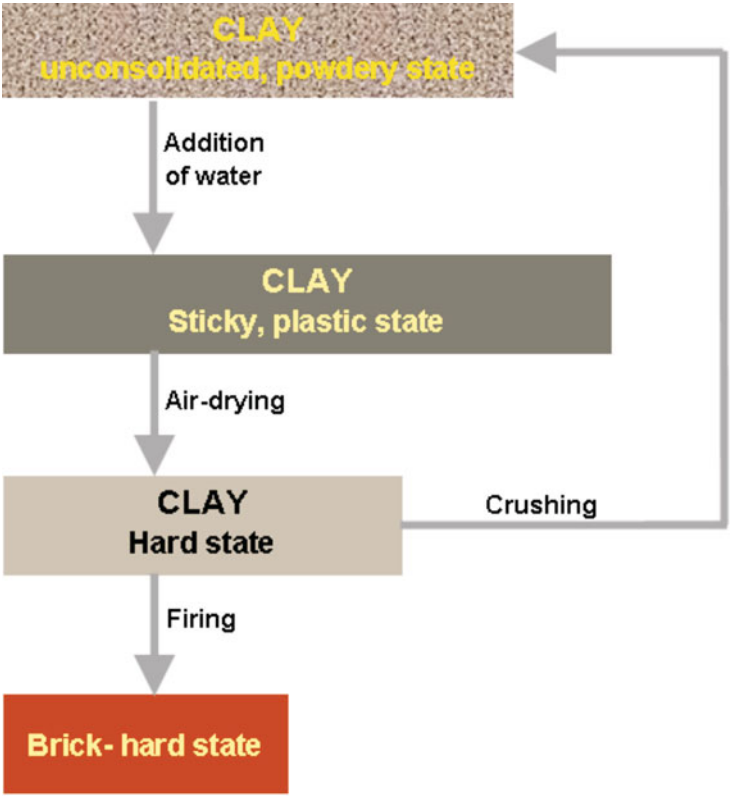

Fig. 1.1: Change of the physical states of clay.

Sometimes the term *clay* is used synonymously with the term *soil*. In addition, Moore (1996) commented that clay is used in three different ways: as a size term, as a rock term and as a mineral term. Now that we have a clear and definite idea about what clay is, the confusion regarding such varied use of this term may be cleared.

- **Soil and Clay:** Soil can be defined as: *collection of natural bodies of the Earth's surface, made up of mineral matters, organic materials, water and air. It contains living matter and supports or is capable of supporting plants*. The proportions of the constituents of soil are given in Fig. 1.2. The mineral matters present in the soil are very fine sized, and many of them are present in clays also. For this reason, some types of soil have considerable plasticity and harden upon drying and firing. But in addition to those minerals, soil also consists of some other minerals, some silt and sand-sized particles, decomposed organic substances (humus) and living matters. Therefore soil should be considered as: *clay mixed with other substances and living matters,* and not as a synonym of clay.

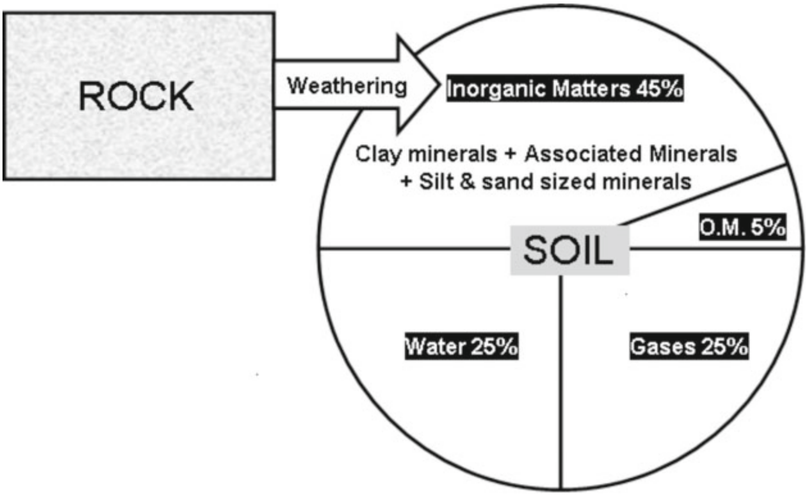

Fig. 1.2: Constituents of soil. Unstable minerals in rock are transformed by *weathering* (see section 1.4.2) to stable inorganic matters which are the chief constituents of soil. Soil also contains organic matters (O.M.), water and gases.

- **Clay as a rock term:** Using clay as a rock term may create confusion, because clays are generally unconsolidated while rocks are essentially rigid. Lithification, diagenesis etc. transform clays to *pelitic rocks* like *shale, claystone* etc. which are indurate and rigid, not plastic like clays. So clay should not be used as a rock term. The position of clay in rock cycle is shown in Fig. 1.5.
- **Clay as a size term:** It is not uncommon in sedimentology to refer all sediments having grainsize <1/256 mm (<4 μm) as clays. But such a usage does not conform to the definition of clay, since all materials of that grainsize are not plastic or do not harden on drying or firing. The use of clay as a size term is therefore not acceptable.
- **Clay as a mineral term:** Guggenheim and Martin (1995) categorically differentiated between clay and *clay minerals*. Clay is composed of various minerals (discussed in the next subsection), so the use of clay as a mineral term is not preferred, and these two terms are not to be used synonymously or interchangeably.

1.2 THE CONSTITUENTS OF CLAY

Clays, like most other solid components of the Earth's crust, are largely made up of one or more mineral species. A mineral species is defined as:

A naturally occurring, inorganic, homogeneous solid, having a definite (but not necessarily fixed) chemical composition and a fixed, ordered internal structure.

When a mineral is produced in favourable condition, its ordered internal structure is reflected in its external morphology and the mineral has a *crystalline* form. Otherwise a mineral is *cryptocrystalline*, i.e. the crystalline form is not perceptible externally but can be detected by scientific analyses like X-Ray Diffraction. Amorphous natural solids like coal, volcanic glasses etc. do not qualify as minerals.

A number of mineral species having similar chemical composition or internal structure constitute a mineral *group.* A number of groups, based on structural or chemical resemblances, constitute one mineral *subclass*. A number of mineral subclasses form a mineral class, which is the highest hierarchical unit in mineral classification. All the minerals belonging to a particular mineral class have the same dominant anion or anionic group. The complete hierarchical order in the classification scheme of minerals is given below:

Same anionic group: **CLASS**
+ *Structural/chemical similarity:* **SUBCLASS**
+ *Chemical/structural similarity to greater degree:* **GROUP**
+ *Solid solution relationship:* **SERIES**
Having a fixed, ordered internal structure: **SPECIES**

J.D. Dana classified the minerals into following anionic classes:

I Native Elements
II Sulphides
III Oxides and hydroxides
IV Halides
V Carbonates, nitrates, borates
VI Sulphates, chromates, molybdates
VII Phosphates, arsenates, vanadates
VIII Silicates

The minerals belonging to *silicate, oxide* and *hydroxide* classes are abundant in the Earth's crust. Some of them that are highly stable in the environment prevailing over or near the earth's surface are the main mineral constituents of clays, since the clays are formed and occur in this environment. The *mineral constituents* of clay may be divided into the following two types:

- **Clay minerals:** They impart plasticity to clay and harden upon drying or firing. Examples: kaolinite, montmorillonite, illite, vermiculite, palygorskite etc.
- **Associated minerals:** These mineral constituents do not impart plasticity to clay. Examples include silicate minerals like micas, quartz, feldspars etc.; iron oxides and hydroxides like magnetite, hematite, maghemite, goethite, lepidocrocite etc.; and aluminium oxides and hydroxides like corundum, gibbside, boehmite, diaspore etc.

In addition to these, most clays contain some amorphous substances and/or organic substances. These non-mineral constituents are known as *Associated Phases*.

The constituents of clay are diagrammatically shown in Fig. 1.3.

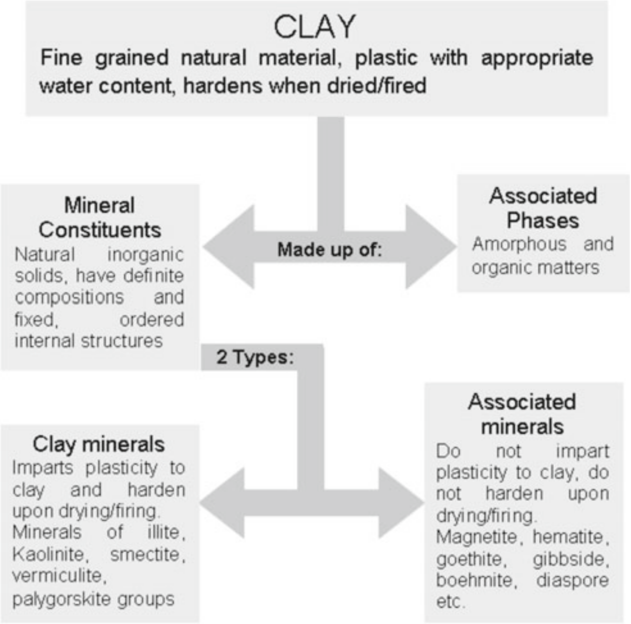

Fig. 1.3: The constituents of clay.

1.2.1 Clay Minerals

Guggenheim and Martin (1995) recommended the following definition of clay minerals for the Joint Nomenclature Committee of AIPEA and CMS:

The term “clay mineral” refers to phyllosilicate minerals and to minerals which impart plasticity to clay and which harden upon drying or firing.

Some important aspects of the above definition of clay minerals are discussed below.

(a) Like all minerals, a clay mineral is also a natural substance. Any synthetic material having the above properties is not a clay mineral. Similarly, any amorphous constituent of clay, even if it imparts plasticity or hardens upon drying and firing, does not qualify as a clay mineral.

(b) The presently known clay minerals belong to phyllosilicate subclass of silicate class (Table 1.1). Basic structural unit of all silicate minerals is the SiO_4^{-4} tetrahedron in which each Si^{+4} is surrounded by four O^{-2} ions in tetrahedral coordination. Each SiO_4^{-4} tetrahedron has unbalanced negative charge, which can be neutralized by bonding with cations (Mg^{+2}, Fe^{+2}, Al^{+3} etc.) and/or by linking of two or more tetrahedra. The silicate class is subdivided into a number of subclasses based on the linking and internal arrangement of the SiO_4^{-4} tetrahedra. In the nesosilicate subclass, each SiO_4^{-4} tetrahedron is isolated, not linked to one another. In sorosilicates, two tetrahedra are linked together. In cyclosilicates 3, 4 or 6 tetrahedra are linked together to form a ring-like arrangement. In inosilicates many tetrahedra are linked together to form a chain-like arrangement. In phyllosilicates, many tetrahedra are linked together to form a two-dimensional sheet-like arrangement. In tectosilicates, many tetrahedra are linked together to form a three-dimensional framework.

In the minerals of phyllosilicate subclass, each SiO_4^{-4} tetrahedron is linked to three adjacent tetrahedra to form an extensive sheet of tetrahedra. Each tetrahedron in that sheet thus shares three (out of four) apical oxygens, having the basic formula unit $Si_2O_5^{-2}$. The phyllosilicate subclass is further subdivided into some groups like mica, chlorite, talc, serpentine, kaolinite, smectite etc. The groups in which clay minerals belong are given in Table 1.1.

Table 1.1 The classification of clay minerals and their positions in the mineral world

Mineral class	*Mineral subclass*	*Mineral groups*	*Mineral species*
SILICATE Contains SiO_4^{-4} tetrahedron as basic structural unit	Phyllosilicate SiO_4^{-4} tetrahedra are linked together to form two-dimensional sheet-like structure	*Kaolinite* (Serpentine-kaolin)	Kaolinite, Dickite, Nacrite, Halloysite, Lizardite, Amesite, Berthierine, Cronstedtite, Nepouite, Kellyite, Fraipontite, Brindleyite
		Smectite (Montmorillonite)	Montmorillonite, Beidellite, Nontronite, Volkonskoite, Saponite, Hectorite, Sauconite, Stevensite, Swinefordite
		Illite (Interlayer-deficient)	Illite, Glauconite, Brammallite, Wonesite
		Vermiculite	Trioctahedral vermiculite, Dioctahedral vermiculite
		Palygorskite-Sepiolite	Palygorskite, Sepiolite, Loughlinite, Falcondoite, Yofortierite
		Mixed Layer (Inter-stratified)	Brinrobertsite, Aliettite, Kulkeite, Rectorite, Hydrobiotite, Corrensite, Tosudite

The group-names used in this book are given in italics and synonyms of the same groups in parentheses. The compositions of clay mineral species are given in next chapters.

(c) Clay minerals are not restricted, by definition, to phyllosilicates. In future, if some non-phyllosilicate mineral is detected in clay that imparts plasticity and hardens upon drying or firing, that mineral will also qualify as a clay mineral.

(d) If future researches reveal a mineral that has high plasticity and hardens upon drying and firing, but is not stable in the natural condition prevailing in the Earth's surface and thus cannot be present in the clays, then it will not qualify as a clay mineral, since contrary to the above definition, it does not *impart plasticity to clay*. Therefore a mineral, to qualify as a clay mineral, must be a constituent of natural clay.

1.2.2 Associated Minerals

Some silicate oxides and hydroxides are stable in the environment prevailing at or near the Earth's surface, and they are resistant to chemical weathering (discussed in section 1.4.2). These minerals, when pulverised to very fine grainsize by natural processes, can be present as associated minerals in the clays. These minerals are not plastic when wet or harden by drying or firing; neither do they impart these properties to the clay. On the contrary, the plasticity of clay decreases as the proportion of associated minerals increases in them. Some associated minerals, especially the oxides and hydroxides of iron, impart to clay some red or reddish-brown colour, which even persists after firing of those clays. Thus the increase of associated minerals decreases the economic value of clay. Some common associated minerals are listed in Table 1.2.

Table 1.2: Associated minerals – their classification and chemical compositions

Mineral class		*Associated mineral species*
Oxides and hydroxides		Hematite: Fe_2O_3 Goethite: FeO(OH) Lepidocrocite: FeO(OH) Limonite: $FeO(OH)\cdot nH_2O$ Corundum: Al_2O_3 Gibbsite: $Al(OH)_3$ Boehmite: AlO(OH) Diaspore: AlO(OH)
Silicates		
	Phyllosilicate subclass	Talc: $Mg_3Si_4O_{10}(OH)_2$ Pyrophyllite: $Al_2Si_4O_{10}(OH)_2$ Chlorite group minerals Muscovite: $KAl_2(Si_3Al)O_{10}(OH,F)_2$
	Tectosilicate subclass	Quartz: SiO_2 Feldspar group minerals

1.2.3 Associated Phases

Clay minerals and associated minerals are essentially inorganic and crystalline (at least, their crystallinity must be detected by X-Ray diffraction). For this reason, some common constituent of clay could not be included in either of the above groups, regardless of their plasticity or other properties. They belong to a third group of clay constituents, termed as associated phases. Guggenheim (1995) considered the following materials as associated phases:

Amorphous materials like allophone, imogolite etc. Crystallinity cannot be detected by X-Ray diffraction in them.

Organic materials, like peat, muck, humus (an important constituent of soil) etc.

1.3 OCCURRENCE OF CLAY MINERALS IN NATURE

Clay minerals are the chief constituents of clays, and they also occur in significant proportions in other earth materials, as illustrated in Fig. 1.4. The

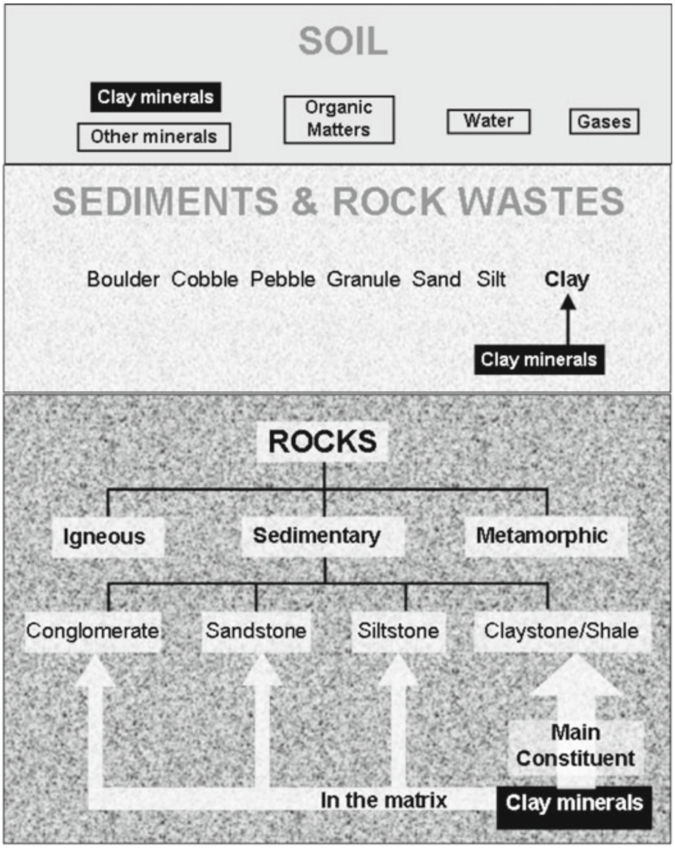

Fig. 1.4: Occurrence of clay minerals in the nature.

land surface of the Earth is covered at most places by a thin veneer of soil, composed of the very fine mineral particles, water, gases and organic matters. Clay minerals are the most important mineral constituents of soils, along with other minerals like quartz, feldspars, micas, chlorites and hydrated iron/aluminium oxides (limonite, hematite, goethite, diaspore, gibbsite etc.).

The soil layer is underlain by a layer of unconsolidated sediments and rock fragments (regoliths). The classification of sediments based on grainsize is given in Table 1.3. Majority of clay-sized sediments are clay minerals.

Table 1.3: Grainsize classification of sediments

Sediments	*Boulder*	*Cobble*	*Pebble*	*Granule*	*Sand*	*Silt*	*Clay*
Grainsize (mm)	>256	256 – 64	64 – 4	4 – 2	2 – 1/16	1/16 – 1/256	**<1/256**

Below the layer of sediments and rock wastes there exists the thick rigid layer of rocks that continues up to the base of Earth's crust. Rocks are of three principal types: igneous, metamorphic and sedimentary. Clay minerals make up about 40% of all the minerals in sedimentary rocks (Nelson, 2011: Web reference). They are the principal constituent of fine-grained sedimentary rocks like mudstone, claystone and shale, where their proportion exceeds 60%. They are also abundant in the matrix of coarser-grained sedimentary rocks like conglomerate, sandstone, siltstone etc. Some clay minerals may occur in low grade metamorphic condition, so they are present in low-grade metasedimentary rocks like slate. But they are gradually transformed to chlorite, muscovite and other minerals as the grade of metamorphism increases. For this reason clay minerals are rare in high grade metamorphic rocks like mica schist.

1.4 FORMATION OF CLAY MINERALS IN NATURE

In any geological environment the clay minerals may come from the following three sources (Millot, 1970; Eberl, 1984).

- They can accumulate from parent rocks without any significant change. This phenomenon is known as *inheritance.*
- They can be synthesized from other minerals or amorphous materials through chemical reactions, and precipitate from solution. This phenomenon is known as *neoformation.*
- They can be produced by alteration of inherited or neoformed clay minerals. This is known as *transformation.*

The genesis, transformation and destruction of clay minerals occur in a cyclic process in nature, as shown in Fig. 1.5. Clay minerals in any natural setting are inherited mostly from fine grained sedimentary rocks and less commonly from coarser sedimentary rocks and low grade metamorphic rocks;

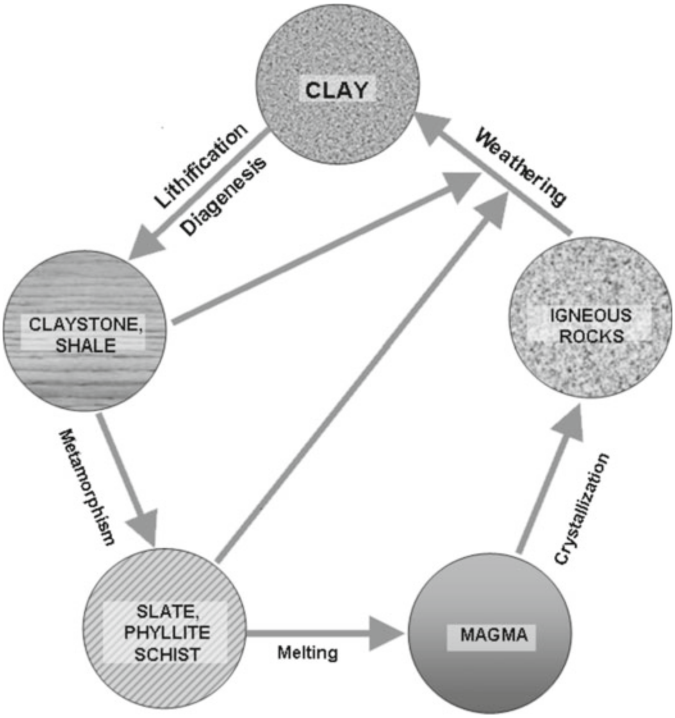

Fig. 1.5: Processes of genesis, transformation and destruction of clay minerals in nature. Clay minerals occurring in clay are produced by rock weathering, transformed during diagenesis, and destroyed by metamorphism. These processes are discussed in section 1.4.2.

and neoformed through *weathering* and *hydrothermal alteration* of different types of igneous, metamorphic and sedimentary rocks.

When the unconsolidated, plastic clays are deposited in a sedimentary basin as pelitic sediments, they are transformed to rigid, brittle pelitic rocks by *diagenesis*. Claystones and mudstones are non-laminated pelitic rocks, and shales are laminated pelitic rocks. During diagenesis, some new clay minerals may appear through transformation of pre-existing clay minerals and neoformation of some non-clay silicate minerals.

At high pressure and temperature, pelitic rocks are metamorphosed to form metapelites. Slate, phyllite and schist are produced successively as the grade of metamorphism increases. Clay minerals are not stable in the high pressure and temperature condition of metamorphism and are gradually transformed to other minerals.

Further increase of temperature melts the rocks to produce magma, which upon cooling and crystallization produce the igneous rocks. The rocks are weathered to form clay again.

The next subsections describe the factors and processes responsible for neoformation and transformation of clay minerals.

1.4.1 Stability of Minerals in Surface and Near-surface Condition

Each mineral is stable within a certain range of pressure and temperature and a definite chemical environment. A mineral outside its stability field is transformed to some other mineral by structural and/or chemical changes, or exists in metastable condition. Many silicate minerals occur in the rocks that form deep inside the Earth's crust where the temperature and pressure are very high, without any free oxygen or free water. Those rocks may be uplifted by some geological processes and brought on or near the Earth's surface, where the physico-chemical environment is characterised by much lower temperature and pressure, and much higher contents of free water and free oxygen.

Because of these differing conditions, minerals in rocks are transformed to new minerals that are stable at the surface or near-surface conditions. Table 1.4 shows the relative stability of minerals in that environment.

Table 1.4: Relative stability of minerals in surface or near-surface environments

Stability Increases	1. Oxides and hydroxides of iron and aluminium
↑	2. Quartz
	3. Clay minerals
	4. Muscovite
	5. Alkali feldspar
	6. Biotite
	7. Amphiboles
	8. Pyroxenes
	9. Ca-rich plagioclase
	10. Olivine

1.4.2 Geochemical Processes of Neoformation and Transformation

As shown in Table 1.4, clay minerals and associated minerals are highly stable in the condition prevailing at the Earth's surface, so they are produced slowly by the reaction of unstable minerals with water and atmospheric gases through various geochemical processes like chemical weathering, diagenesis, hydrothermal alteration etc. A brief outline of these processes and the role they play in the formation of clay minerals are given here.

(a) Chemical Weathering

It is the breakdown (decay/decomposition) of rock by chemical reactions at normal temperature and pressure condition. In these reactions dilute solvents like carbonic acid and other acids migrate through the rock and react with the minerals that are relatively unstable in surface condition, to produce clay minerals, associated minerals and other stable materials. The following types of chemical weathering reactions are important in the formation of clay minerals and associated minerals:

Hydrolysis: It is an exchange reaction involving minerals and water. The hydrogen (H^+) and hydroxyl (OH^-) ions from the water replace the metallic cations of the mineral (K^+, Na^+ etc.), giving rise to leaching out of those cations and the formation of metallic cation deficient, hydrous minerals. By this process the silicate minerals like potassium feldspar [$KAlSi_3O_8$] are transformed to clay minerals like illite [$K_nAl_2Si_2O_5(OH)_4$, $n = 1$ to 1.5] by partial leaching out of K^+, or to kaolinite [$Al_2Si_2O_5(OH)_4$] by complete removal of K^+.

$$2KAlSi_3O_8 + 2H^+ + 9\ H_2O = K_nAl_2Si_2O_5(OH)_4 + 4H_4SiO_4 + (1 - n)K^+$$

$$2KAlSi_3O_8 + 2H^+ + 9\ H_2O = Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2\ K^+$$

Oxidation: It takes place when oxygen reacts with earth materials. Oxygen dissolved in water combines with atoms of metallic elements of silicate minerals. When oxygen combines with iron, the *hematite* (Fe_2O_3) which is a common associated mineral is formed:

$$4Fe^{+3} + 3O_2 = 2Fe_2O_3$$

Hydration: It is the introduction of water molecules in the mineral structure to form hydrous minerals. Example: the conversion of hematite to limonite:

$$Fe_2O_3 + H_2O \longrightarrow FeO(OH)\cdot nH_2O$$

(b) Diagenesis

It is a series of chemical and physical changes in deposited sediments that convert them to sedimentary rock. Weathering and erosion of rocks produce loose, unconsolidated materials. These materials, after being deposited, are subjected to diagenesis and transformed to indurated sedimentary rocks. Diagenesis takes place in subsurface condition at temperature and pressure higher than those of weathering but lower than those of metamorphism.

Diagenesis involves the following physical and chemical processes:

(i) Compaction: It is the decrease of the volume of a buried sediment mass due to the weight of overlying materials. Major part of pore water of the sediments is expelled during compaction.

(ii) Recrystallisation: It is the change of crystal fabric in a mineral without change in composition.

(iii) Dissolution and replacement: Unstable minerals are dissolved into a solution or replaced by a stable mineral.

(iv) Authigenesis: It is the formation of a new mineral in the diagenetic environment, which is precipitated in the pore spaces.

(v) Cementation: If sufficient quantity of new minerals are precipitated in the pore spaces, the unconsolidated sediments are cemented together to form the indurate rock.

The clay minerals are formed, modified and converted to other minerals during different stages of diagenesis. In the late stage of compaction, water molecules from the lattice of clay minerals are expelled, bringing about considerable change in their structures. Some minerals of kaolinite and smectite group are formed during authigenesis. During deep burial diagenesis, one clay mineral may be transformed to another with the increase of temperature, through expulsion of water molecules and incorporation of cations (like K^+) in the lattice. As temperature increases, smectite is slowly and gradually transformed to mixed layer clay minerals and illite. Similarly, kaolinite is transformed to dickite and nacrite. Above 100°C, kaolinite and smectite are fully transformed to illite and chlorite (Tucker, 1981).

(c) Hydrothermal Alteration

It is the mineralogical, chemical and textural changes of the rocks by hydrothermal liquids (high temperature aqueous solutions), generally taking place below the surface at 50°C to 500°C.

High temperature subsurface water leaches out ions and minerals from the rocks in its contact, and turns into a hot aqueous solution known as hydrothermal solution. It rises through cracks and fractures and picks up dissolved minerals and elements on its way, thus altering the original minerals of the rock to form new minerals. Generally the cations of the original minerals are partly leached out by the hydrothermal liquid, and water molecules enter their structures. Consequently cation-deficient hydrous minerals are formed, a sizeable portion of which are clay minerals. Examples include the formation of halloysite deposits by low temperature hydrothermal alteration of volcanic ash of Northland, New Zealand (Harvey and Murray, 1993); and formation of hectorite by hydrothermal alteration of Li^+-Mg^{+2} rich basaltic ash (Harvey and Lagaly, 2006).

1.4.3 Clay Mineral Paragenesis

The minerals with resembling chemical composition and internal structure are likely to occur together in nature, and they are generally formed in the same geological environment. When some minerals originate in the same geological environment and occur in contact of one another, they affect one another's formation. Paragenesis of a mineral refers to the characteristic association and occurrence of that mineral in a well-defined geological environment. The paragenesis of the clay minerals is described here.

(a) Kaolinite

It is primarily formed by weathering or low-temperature hydrothermal alteration of feldspars, muscovite and other Al-rich silicates of acidic igneous rocks (granite, rhyolite, quartz diorite etc.). Hydrolysis is the chemical weathering reaction that brings about this transformation.

$$2KAlSi_3O_8 + 3H_2O = Al_2Si_2O_5(OH)_4 + 4SiO_2 + 2\ KOH$$

KOH and silica produced by the above reaction are leached away, and kaolinite occurs as residual deposits. If all the K^+ is not separated, then illite is formed instead of kaolinite.

Kaolinite also occurs as secondary deposit where it or its parent minerals are transported under suitable non-alkaline condition and deposited in deltaic, lagoonal or other non-marine environment.

Most sedimentary kaolinite is detrital in origin and forms in the soil. But it is also found in mudrocks, clastic sediments and coal as an authigenic mineral, formed at shallow depth where temperature is low.

(b) Illite

It is one of the most abundant mineral in sedimentary rocks and also found in some low grade metamorphic rocks. It is formed by the following two processes:

(i) Neoformation through weathering of feldspars and muscovite.
(ii) Transformation of smectite and kaolinite through diagenesis and low-grade metamorphism.

As temperature increases, the lattices of clay minerals lose H_2O molecules. Illite is therefore favoured than smectite at the temperature of diagenesis or low-grade metamorphism.

Illite occurs as fibrous material filling up sandstone pores, with or without smectite. It often replaces kaolinite pseudomorphously. The process of sericitization produces illite from feldspar at lower part of weathering zones. Illitization also takes place in hydrothermal environments around ore deposits.

(c) Smectite

It is generally formed in the sedimentary deposits by transformation of other clay minerals or non-clay minerals by diagenetic or hydrothermal processes. It may also form by neoformation from solution to colloids.

Smectite group minerals, when present in the petroleum reservoirs, play an important role in the migration of hydrocarbons. At the shallow level of reservoir rocks smectite can exist, but at deeper level the increase of temperature transforms it to other minerals. Generally dioctahedral smectites are transformed to illite and trioctahedral smectites are transformed to chlorite, releasing the interlayer water molecules in both cases. That released water increases the pore fluid pressure that may lead to migration of the hydrocarbons.

Smectites also occur as hydrothermal alteration products around metalliferous veins or deposits, and near hot springs and geysers.

Montmorillonite and beidellite: In bentonite clay, they are formed by weathering of extrusive igneous rocks like tuffs, volcanic ash etc. In Fuller's earth, montmorillonite is produced by the weathering of basic igneous rocks, or occurs in the sedimentary products derived from them.

Nontronite: It is neoformed as follows:

(i) As authigenic clay minerals in recent submarine sediments
(ii) As hydrothermal precipitates from the hot brines at mid-oceanic ridges
(iii) As weathering products of basalt, ultrabasic rocks and volcanic glass.

Sauconite: This zinc-smectite occurs around ore bodies of zinc and in laterites.

Saponite: It is commonly formed from weathering of basic volcanic materials. It sometimes fills up the vesicles of basalt, forming the amygdales.

Hectorite: It is formed by hydrothermal alteration of pyroclastic materials.

(d) Vermiculite

The major commercial deposits of vermiculite are neoformed by weathering or hydrothermal alteration of biotite of large bodies of basic and ultrabasic rocks. Other mafic minerals present in those rocks, like phlogopite, chlorite, pyroxene etc. also participate in the reaction.

Biotite present in metamorphic rocks like gneiss, schist etc. may also be altered to form vermiculite. In marine sediments, alteration of mica to vermiculite is relatively rare, since the K^+ of sea water readily alter it.

(e) Palygorskite and Sepiolite

Palygorskite and sepiolite occurring in soils are generally neoformed under dry or semi-dry climates. These minerals are less stable in wet climates.

Transformation and inheritance played important roles in the formation of some large palygorskite deposits of the world: the major part of palygorskite was produced by S*mectite* → *Palygorskite* transformation in shallow marine environment and the rest was detrital palygorskite from the continent. In some cases, palygorskite is neoformed by alteration of basalts in an alkaline environment.

Sepiolite is largely neoformed, mainly produced by direct precipitation in saline lacustrine environments. It may occur with other Mg^{2+}-rich clay minerals.

1.5 DIFFERENT TYPES OF CLAYS

The composition, origin and uses of some common types of clays and argilloids are given below.

(a) **Primary Kaolin:** This type of clay is predominantly composed of kaolinite. It is highly plastic, shrinks and hardens under firing and under air drying, cohesive and absorbent of water and oil. It is used in porcelain industry, in medicine, in paper as filler, in toothpaste and cosmetics as additive, in light bulbs as light diffusing material, in paint to modify gloss levels, in rubber as reinforcing agent; and in adhesives to modify the viscosity.

(b) **Secondary Kaolin:** It has similar composition, properties and uses like primary kaolin and differs with respect to origin – while primary kaolin is produced from hydrothermal alteration of granitic rocks, secondary kaolin has authigenic sedimentary origin.

(c) **China Clay:** This type of clay is largely composed of kaolinite, but its plasticity is less than primary or secondary kaolin. It is white when fired at high temperature. It is formed by hydrothermal alteration and has uses similar to kaolin.

(d) **Ball Clay:** Kaolinite is the main constituent of this clay, though the quantity of associated mineral is greater than that of kaolin. It is plastic, easily mouldable and is white or near-white when fired at high temperature. It is used in pottery, tableware, washbasins and toilet bowls, wall and floor tiles, electrical insulators and other ceramics, pencil industry etc.

(e) **Fire Clay:** Kaolinite of authigenic sedimentary origin is the main constituent of this type of clay, though other clay minerals and associated minerals are present in higher proportion than kaolin, china clay and ball clay. It is plastic and resistant to high temperatures, having fusion points higher than 1600°C. It is mainly used in the production of fire bricks for lining furnaces and also in the manufacture of utensils used in metalworking industries like crucibles, saggars, retorts etc. Complex pottery items like pipes and sanitary ware are also prepared from it. Presence of metallic oxides in a high proportion imparts in it a colour that makes it unsuitable in the manufacture of high quality ceramics.

(f) **Refractory Clay:** Kaolinite of authigenic sedimentary origin is the main constituent of refractory clay. It is plastic and resistant to high temperatures. It is used in the production of refractory bricks.

(g) **Bentonite:** This type of clay is composed of smectites, mainly montmorillonite. It is formed by hydrothermal alteration of basaltic rocks and also by authigenesis. It is highly plastic, and expands considerably when water is added to it. Relatively small quantities of bentonite suspended in water form a viscous, shear thinning material. They are generally thixotropic, i.e. thick (viscous) under normal conditions, but become less viscous and flow over time when shaken or agitated. It is one of the raw materials in cement industry, and used in the manufacture of some ceramic bodies. Some types of adhesives are prepared from it. Its power of liquid absorption enables its use in cat litter; and its binding properties facilitates its use as a binding agent in the manufacture of taconite pellets for steel industry.

(h) **Bleaching Earth:** It is composed of montmorrilonite produced by alteration of bentonite in acidic environment. It has high adsorption power and expands on absorption of water. It is selectively absorbing; has high de-colouring rate and fast filtering speed, low residual oil. It can adsorb the toxins, pesticide remains and bad smell. Its de-colouring and purifying property is utilised for refining vegetable oils and animal fat. It is also used to purify liquid glucose, maltose, sucrose etc. Its selective absorption power is used to adsorb toxins from fat and vegetable oils and in waste water treatment.

(i) Common Clay: Mainly illite and smectite, with some amount of kaolinite and mixed layer clay are present in it. Chlorite is a commonly present associated mineral. It is a plastic clay, produced mainly by weathering of rocks. It is used for brick, clay pipe, clay floor, wall tiles and drain tiles, and other building materials. It cannot be used in porcelain due to presence of impurities that degrade its quality, but is sometimes used in low-quality ceramic products.

(j) Argilloids – Flint Clay and Fuller's Earth: These materials are not clay by definition since they are not plastic at appropriate water content. We recommend calling these materials *argilloid* (clay-like) instead of *clay.* The following definition may be suggested for it:

An argilloid is a fine-grained material that contains clay minerals in considerable proportions and has some similarities with clay pertaining to origin, and industrial uses, but not plastic when wet.

In flint clay, diagenetically formed kaolinite is the main clay mineral and quartz, siderite, iron oxide etc. are present in considerable proportions. It is non-slaking and non-plastic, and suitable only for use in refractories.

Fuller's earth contains montmorillonite and sometimes palygorskite-sepiolite. Some of the other minerals that may be present in Fuller's earth are calcite, dolomite, and quartz. It has sedimentary, residual and hydrothermal origin. It is a non-plastic, thixotropic material. It has long been used to clean raw wool from grease and dirt. It is also used for decolourizing, filtering, and purifying oils and animal fat.

Concluding Remarks

Comprehensive description of the composition, physical and chemical properties of different types of clays are given in the subsequent chapters of this Part. The industrial uses of these clays and their constituents are systematically described in Part II.

QUESTIONS

1. Give explicit definitions of the following terms: elements, chemical compounds, organic compounds, inorganic compounds, mechanical admixtures, solutions, crystalline substances, amorphous substances, homogeneous substances, inhomogeneous substances, minerals and rocks. In which of the above categories the following substances belong? Explain with reasons. (A particular substance given below may belong to more than one of the above categories.)

   (a) Clay
   (b) Clay mineral
   (c) Associated mineral
   (d) Associated phase
   (e) Claystone and shale
   (f) Soil

2. Putty, plasticine and the modelling clays used by artists are composed of fine grained materials, and they are highly plastic. Do they qualify as clays? Justify.
3. Is it justified to use the terms soil and clay interchangeably? Explain with reasons.
4. Which attributes of clay facilitate its use in pottery and modelling?
5. Why the term argilloid is introduced in the present work?
6. Explain the justification of using clay as a rock term.
7. A substantial proportion of fine grained quartz, micas and feldspar group minerals are present in many types of natural clays, still these minerals are not considered as clay minerals. Why? What would be the possible effect of the increase of the proportion of these minerals in a clay?
8. How the clay minerals of smectite group play an important role in the migration of hydrocarbons in petroleum reservoirs?
9. In what natural condition the formation of palygorskite and sepiolite takes place and why?
10. Explain why vermiculite is relatively rare in marine sediments.
11. The clay tea-cups are widely used in all parts of India. They are produced by moulding common clay into the shape of cups, and then heated to get the hardened, water-resistant material. Discuss the acceptability of such tea-cups from environmental point of view, and compare them with plastic and paper tea-cups.

FURTHER READING

Bergaya, F., Theng, B.K.G. and Lagaly, G. (2006). Clays in Industry. *In:* Bergaya, F., Theng, B.K.G. and Lagaly, G. (Eds), Handbook of Clay Science. Elsevier, Amsterdam.

Deer, W.A., Howie, R.A. and Zussman, J. (1992). An introduction to the rock forming minerals. English Language Book Society with Longman.

Eberl, D.D. (1984). Clay mineral formation and transformation in rocks and soils. *Phil. Trans. R. Soc. Lond. A*, **311:** 241-257.

Folk, RL. (1974). Petrology of sedimentary rocks. Hemphill Publishing Co., Texas.

Guggenheim, S. and Martin, R.T. (1995). Definition of clay and clay mineral. Joint report of the AIPEA nomenclature and CMS nomenclature committees. *Clays and Clay Minerals*, **43(2):** 255-256.

Guggenheim, S. and Martin, R.T. (1996). Reply to the comment by D.M. Moore on “Definition of clay and clay mineral: Joint report of the AIPEA nomenclature and CMS nomenclature committees”. *Clays and Clay Minerals*, **44(5):** 713-715.

Guggenheim, S., Adams, J.M., Bain, D.C., Bergaya, F., Brigatti, M.F., Drits, V.A., Formoso, M.L.L., Galan, E., Kogure, T. and Stanjek, H. (2006). Summary of recommendations of nomenclature committees relevant to clay mineralogy: Report of the Association Internationale pour l'Etude des Argiles (AIPEA) Nomenclature Committee for 2006. *Clays and Clay Minerals*, **54:** 761-772.

Harvey, C.C. and Lagaly, G. (2006). Conventional Applications. *In:* Bergaya, F., Theng, B.K.G. and Lagaly, G. (Eds), Handbook of Clay Science. Elsevier, Amsterdam.

Harvey, C.C. and Murray, H.H. (1993). The geology, mineralogy and exploitation of halloysite clays of Northland, New Zealand. *In:* Murray, H.H., Bundy, W.M. and Harvey, C.C. (Eds), Kaolin Genesis and Utilization. The Clay Minerals Society.

Klein, C. (2002). Mineral Science. John Wiley & Sons, Inc.

Mason, B.H. and Moore, C.B. (1982). Principles of Geochemistry, Wiley.

Millot, G. (1970). Geology of Clays. Translated by W.R. Farrand and H. Paquet. Springer Verlag.

Moore, D.M. (1996). Comment on: Definition of clay and clay mineral: Joint Report of the AIPEA Nomenclature and CMS Nomenclature Committees. *Clays and Clay Minerals*, **44:** 710-712.

Ollier, C. (1984). Weathering (2nd edition). Geomorphology Texts. Longmans, London.

Tucker, M.E. (1981). Sedimentary petrology: An introduction. Blackwell Scientific Publications.

Velde, B. (1980). Clay minerals: A Physico-Chemical Explanation of their Occurrence. Elsevier.

Web Reference

Nelson, S.A. Weathering & Clay Minerals.

http://www.tulane.edu/~sanelson/eens211/weathering&clayminerals.htm, Last updated 30th Nov. 2011.

CHAPTER

2

CLASSIFICATION AND COMPOSITION OF CLAY CONSTITUENTS

Classification of clays by some rational basis into groups facilitates the convenient studies of its properties and application. Clays belonging to the same group have similarities in physical and chemical properties, and may be related to corresponding industrial and environmental applications. Chemical composition is one of the major criteria for classification of clays, along with internal structures, origin, natural occurrence etc.

2.1 INTRODUCTION

Most of the solid components of the Earth's crust, i.e. rocks, sediments, clays etc. are largely made up of various mineral species. A mineral species is defined as: *A naturally occurring, inorganic, homogeneous solid, having a definite (but not necessarily fixed) chemical composition and a fixed, ordered internal structure, i.e. crystalline*. This ordered internal structure is reflected in the external morphology when the mineral has a well *crystalline* form. When the crystalline form is not perceptible externally called cryptocrystalline, its crystalline nature can be detected by scientific analytical techniques like X-Ray Diffraction. Amorphous natural solids like coal, volcanic glasses etc. do not qualify as minerals. The abundance of any mineral in the Earth is decided by the availability of the constituent elements of the mineral in the earth's crust and also the stability of that mineral in the surface or near-surface environment.

Silicon and oxygen being the most abundant elements of Earth crust, *silicate, oxide* and *hydroxide* class of minerals are most commonly available

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there. Mineral classes are identified (anionic) by J.D. Dana as (i) Native elements, (ii) Sulphides, (iii) Oxides and hydroxides, (iv) Halides, (v) Carbonates, nitrates, borates, (vi) Sulphates, chromates, molybdates, (vii) Phosphates, arsanates, vanadates and (viii) Silicates.

The mineral groups are identified with similar chemical composition or internal structure e.g. when chemical composition is considered, both calcite ($CaCO_3$) and aragonite ($CaCO_3$) belong to the carbonate group. But, when crystal structures are considered, calcite belongs to Calcite group with many other carbonate minerals, like magnesite ($MgCO_3$), siderite ($FeCO_3$) etc. having similar hexagonal crystal structure. On the other hand, aragonite with orthorhombic crystal structure, belongs to aragonite group with cerrusite ($PbCO_3$) and strontianite ($SrCO_3$) etc.

Several groups with structural and chemical similarities are bunched together as mineral subclass. In silicate minerals the basic silica tetrahedral may form rings, sheets etc. forming different mineral subclasses like sorosilicates, sheet silicates etc. And the silicate subclass forms a mineral class. A particular mineral class have the same anion or anionic groups.

A prolonged weathering, erosion and disintegration of rock materials over the surface of Earth produce clays. The constituent minerals of clays are highly stable in the surface environment and resistant to chemical weathering. Clays may also contain a non-mineral part, e.g. amorphases and organic matter.

The clay constituents can be described as shown in Fig. 2.1.

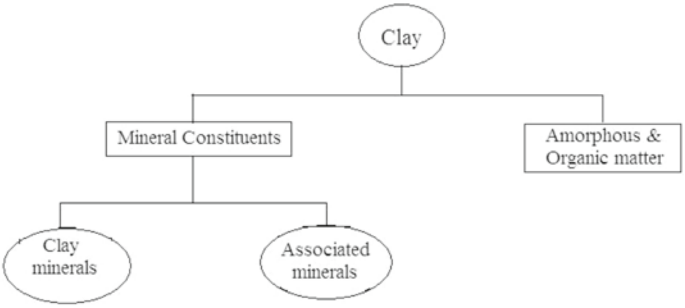

Fig. 2.1: Constituents of clay.

Table 2.1: Properties of clay and associated minerals

Minerals	*Properties*	*Drying/firing*	*Examples*
Clay minerals	Import plasticity	Hardens on drying/firing	Kaolinite, montmorillonite, illite, vermiculite, palygorskite etc.
Associated minerals	Do not import plasticity		Magnetite, hematite, maghemite, goethite, lepidocrocite gibbside, boehmite, diaspore.

2.2 CLASSIFICATION OF CLAY MINERALS

Clay minerals belong to the phyllosilicate subclass of silicate class. They have been abundantly studied by X-ray diffraction, which is the basic tool for their identification as it is difficult to observe without using electron microscope.

Let us know first about the silicate minerals and then the clay minerals in the silicate group. All silicate minerals have the anionic group $[SiO_4]^{-4}$ consisting of one Si^{+4} surrounded by four O^{-2}. The tetrahedron obtained by joining the centres of the four O^{-2} is known as $[SiO_4]^{-4}$ tetrahedron.

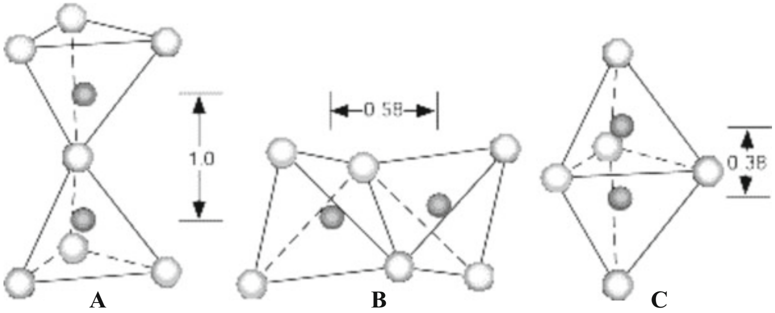

Fig. 2.2: Sharing of apical oxygen between SiO_4^{-4} tetrahedra. **A** (corner sharing) is stable. **B** (side sharing) and **C** (edge sharing) are not stable.

Each $[SiO_4]^{-4}$ tetrahedron has an unbalanced charge of – 4, which can be neutralized in the following two ways:

- **Bonding with cations:** An SiO_4^{-4} tetrahedral group can be bonded to cations. Generally bivalent cations like Mg^{+2}, Fe^{+2}, Ca^{+2} etc. are bonded to the tetrahedral group in common silicate minerals. The monovalent cations like Na^+, K^+ and the trivalent cations like Fe^{+3}, Al^{+3} etc. are also common.
- **Linking of tetrahedra:** Two or more tetrahedra can be linked together by their apical oxygens. The O^{-2} that links two adjacent tetrahedra is known as *bridging oxygen*, and its charge is shared by two Si^{+4}. Different arrangements of linking of apical oxygens give rise to the different silicate subclasses, as discussed in Table 2.2.

Table 2.2: Description of some elements

Elements	*Description*
Apical oxygen	The unpaired oxygen in a tetrahedral sheet. These oxygens lie in a plane.
Basal oxygen	Any of the three shared oxygens in the tetrahedral sheet.
Sheet	The planes of atoms associated with either the Si/Al tetrahedra or the octahedra. Oxygens lying in the plane between the plane of Si and the plane of Al atoms are bonded to both sets of cations and are considered to be members of both sheets.

Subclass Nesosilicate: In this subclass, no apical oxygen of one SiO_4^{-4} tetrahedron is shared with other SiO_4^{-4} tetrahedra, i.e. no bridging oxygen in the tetrahedron. In this group the oxygens are shared with octahedral groups that contain other cations like Mg^{+2}, Fe^{+2} or Ca^{+3}. Common examples are olivines, garnets, Al_2SiO_5 minerals (andalusite, kyanite and sillimanite), staurolite, and sphene.

Subclass Sorosilicate: In this case, one of the apical oxygens of one tetrahedron is shared with another tetrahedron, i.e. one bridging oxygen in each tetrahedron. The basic structural unit is $Si_2O_7^{-6}$. Example: hemimorphite – $Zn_4Si_2O_7(OH)\cdot H_2O$.

Subclass Cyclosilicate (Ring Silicates): In cyclosilicates, two of the apical oxygens of each tetrahedron are shared with two adjacent tetrahedra, and the linked tetrahedra are arranged in a ring. The ring may be formed by linking of 3, 4, 5 or 6 tetrahedra, forming the structural units $Si_3O_9^{-6}$, $Si_4O_{12}^{-8}$, $Si_5O_{15}^{-10}$ and $Si_6O_{18}^{-12}$ respectively. In each case Si:O ratio is 1:3. Example: beryl – $Be_3Al_2Si_6O_{18}$.

Subclass Inosilicate – Single Chain: In this structure two apical oxygens of each SiO_4 tetrahedron are shared in a way to form a long single chain of linked tetrahedra. The basic structural unit of single chain inosilicates is $Si_2O_6^{-4}$ or SiO_3^{-2} with an Si:O ratio of 1:3. In some cases Al^{+3} can replace Si^{+4} in the tetrahedral site.

Subclass Inosilicate – Double Chain: In the double chain inosilicates, two parallel chains are linked together by their alternate tetrahedra. The basic structural group is $Si_4O_{11}^{-6}$. The amphibole group of minerals are double chain silicates, for example the tremolite-ferroactinolite series – $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_3$.

Subclass Phyllosilicates (sheet silicates): In this structure each SiO_4 tetrahedron is linked to three adjacent tetrahedra to form an infinite sheet of tetrahedra. Each tetrahedron in the sheet thus shares three (out of four) apical oxygens, having the basic structural unit $Si_2O_5^{-3}$. Some Si^{+4} of the tetrahedral site may be replaced by Al^{+3}, and the charge is balanced by inclusion of additional cations. The micas, clay minerals, chlorite, talc and serpentine minerals are examples of phyllosilicates.

Subclass Tectosilicates (framework silicates): The tectosilicates or framework silicates have a structure where all of the four oxygens of an SiO_4^{-4} tetrahedron are shared with four adjacent tetrahedra. The ratios of Si to O is thus 1:3. The basic structural group then becomes SiO_3. The minerals – quartz, cristobalite, tridymite etc. – are based on this structure. If some of the Si^{+4} ions are replaced by Al^{+3}, a charge imbalance is produced which is neutralized by incorporation of other cations in different coordination sites within the framework structure. Thus, the feldspar and feldspathoid minerals are also based on the tectosilicate framework.

The phyllosilicate subclass, like the other silicate subclasses, is divided into a number of groups, based on chemical and structural affinities. The mineral species belonging to six phyllosilicate groups show the properties specified in the definition of clay minerals. They are: kaolinite group, smectite group, illite group, vermiculite group, palygorskite-sepiolite group and mixed layer group.

2.3 ASSOCIATED MINERALS AND PHASES

Some minerals of silicate class and oxide and hydroxide class are stable in the environment prevailing at or near the Earth's surface, and they are resistant to chemical weathering. These minerals, when pulverised to very fine grain size by natural processes, classified as in Table 2.3, can be present as associated minerals in the clays. These minerals are not plastic when wet or harden by drying or firing; neither do they impart these properties to the clay. On the contrary, the plasticity of clay decreases as the proportion of associated minerals increases in them. Some associated minerals, especially the oxides and hydroxides of iron, imparts to clay some red or reddish-brown colour, which even persists after firing of those clays. Thus the increase of associated minerals decreases the economic value of clay. Some common associated minerals are listed below.

Table 2.3: Clay mineral groups

Mineral class	Silicate: SiO_4^{-4} tetrahedron is the basic structural unit of all silicate minerals in which each Si^{+4} is surrounded by four O^{-2} ions in tetrahedral coordination.
Silicate subclass	Phyllosilicate: In the structure of phyllosilicate, each SiO_4 tetrahedron is linked to three adjacent tetrahedra to form an infinite sheet of tetrahedra. Each tetrahedron in the sheet thus shares three (out of four) apical oxygens, having the basic structural unit $Si_2O_5^{-2}$. The micas, clay minerals, chlorite, talc and serpentine minerals are examples of phyllosilicates.

Clay Group

Kaolinite	*Smectite*	*Illite*	*Vermiculite*	*Palygorskite-sepiolite*	*Mixed layer*
Kaolinite, Dickite, Nacrite, Halloysite, Lizardite	Montmorillonite, Beidellite, Nontronite, Hectorite, Sauconite	Illite, Glauconite, Brammallite, Wonesite	Trioctahedral vermiculite, Dioctahedral vermiculite	Sepiolite, Loughlinite, Falcondoite, Palygorskite	Aliettite, Kulkeite, Rectorite

Like iron oxides, Mn-oxides in the form of various mineral species are typical constituents of many clays and are formed by oxidation of Mn^{2+}, contained in low temperature solutions in the hypergene minerals.

Zeolites are microporous, crystalline solids with well-defined structures. Generally they contain silicon, aluminium and oxygen in their framework and cations. Many occur naturally as minerals, and are extensively mined in many parts of the world. Others are synthetic zeolites which have a porous structure that can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite and stilbite. An example of mineral formula is: $Na_2Al_2Si_3O_{10} \cdot 2H_2O$, the formula for natrolite. Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites are widely used in industry for water purification, as catalysts, for the preparation of advanced materials and in nuclear reprocessing. Their biggest use is in the production of laundry detergents. They are also used in medicine and in agriculture.

Laterites, the source of Al-ore exists largly in clay minerals. Gibbsite, bohemite, and diaspore are the Al-hydroxides which provide a major source of Al and Fe ores.

Table 2.4: Name and composition of oxides and hydroxides minerals

Name	*Composition*
Hematite	Fe_2O_3
Maghemite	Fe_2O_3
Goethite	FeOOH
Lepidocrocite	FeOOH
Corundum	Al_2O_3
Gibbsite	AlOOH
Boehmite	AlOOH
Diaspore	AlOOH

Table 2.5: Name and composition of phyllosilicates minerals

Name	*Composition*
Talc	$Mg_3Si_4O_{10}(OH)_2$
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$
Muscovite	$KAl_2(Si_3Al)O_{10}(OH,F)_2$
Chlorite group minerals	

Table 2.6: Name and composition of tectosilicates minerals

Name	Composition
Quartz	SiO_2
Feldspar group minerals	

Table 2.7: Description of sheet silicate (some of which occurs in clay)

Group mineral	*Mineral*	*Formula*	*Crystallography*	*Transparency*
Serpentine	Antigorite	$Mg_6Si_4O_{10}(OH)_{10}$	Monoclinic	Translucent
	Chrysolite	$Mg_6Si_4O_{10}(OH)_{10}$	Monoclinic	Translucent
	Lizardite	$Mg_6Si_4O_{10}(OH)_{10}$	Monoclinic	Translucent
Clay	Montmorillonite	(Ca,Na)0.2-0.4 $(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2.nH_2O$	Monoclinic	Translucent
	Kaolinite	$Mg_3Si_4O_{10}(OH)_2$	Triclinic	Translucent
	Pyrophyllite	$Al_2Si_2O_5(OH)_4$	Triclinic	Translucent
	Talc	$Al_2Si_4O_{10}(OH)_2$	Triclinic	Translucent
	Illite	Mica like clay mineral	Triclinic	Translucent
Mica	Phlogopite	$KMg_3(AlSi_3O_{10})(OH)_2$	Monoclinic	Transparent; In thin sheets
	Annite	$KFe_3(AlSi_3O_{10})(OH)_2$	Monoclinic	Translucent
	Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	Monoclinic	Transparent In thin sheets
	Lepidonite	$K(Li,Al)_{2-3}(AlSi_3O_{10})(OH)_2$	Monoclinic	Translucent
	Margarite	$CaAl_2(Al_2Si_2O_{10})(OH)_2$	Monoclinic	Translucent
Chlorite	Clinochlore	$(Mg_5Al)(AlSi_3)O_{10}(OH)_8$	Triclinic	Transparent
	Chamosite	$(Fe_5Al)(AlSi_3)O_{10}(OH)_8$	Monoclinic	Translucent
	Nimite	$(Ni_5Al)(AlSi_3)O_{10}(OH)_8$	Monoclinic	Translucent
	Pennantite	$(Mn,Al)_6(AlSi)_4O_{10}(OH)_8$	Triclinic	Transparent

Table 2.8: Description of clay mineral group

	Montmorillonite	*Kaolinite*
Origin of name	From its original discovery at Montmorillon, near Limoges, France	The name of hill Chinese Kao-ling was the first source of kaolinite.
Structure and composition	The structure is based on groups of three layers: Single sheet of (Al, Mg) $(O, OH)_6$ octahedra are sandwiched between two sheets of SiO_4 tetrahedra. Montmorillonite is a member of the smectite group and forms solid solution with beidellite.	It is a layer silicate. It has a two-layers structure: Layers of $Al(O,OH)_6$ octahedra alternate with sheets of SiO_4 tetrahedra. Several minor substitutions are possible: Alkalis or alkaline earth may be present, as well as excess H_2O.
Habit	Earthy masses are typical	It is usually massive or a fine grained aggregate: rare platy, pseudohexagonal crystals have been found.
Crystallography	Monoclinic, $a = 5.17$, $b = 8.94$, $c = 15.20$, $\beta = 90°$, $Z = 2$	Triclinic, $a = 5.15$, $b = 8.92$. $c = 7.38$, $\alpha = 90.8°$, $\beta = 104.8°$, $\gamma = 90°$, $Z = 2$

(*Contd.*)

Table 2.8 (*Contd.*)

	Montmorillonite	*Kaolinite*
Hand Specimen Identification	When massive, they are earthy if wet, and appear as soft, very fine grained aggregates if dry.	Clay-like properties, including softness, habit, feel and earthy smell, help identify kaolinite.
Physical properties		
Colour	White, gray	White
Transparency	Translucent	Translucent
Lustre	Dull	Dull
Cleavage	Perfect {001} rarely visible	Perfect (001)
Fracture	Irregular	Rarely seen
Hardness	$1\text{-}1^{1/2}$	$2\text{-}2^{1/2}$
Specific gravity	2.0-2.7	2.6
Optical properties	Optical properties are highly variable due to variable chemistry and crystallinity.	Optical identification of kaolinite is very difficult. Biaxial (-), $\alpha = 1.556$, $\beta = 1.563$, $\gamma = 1.565$, $\delta = 0.007$, $2V = 40°$
Occurrence and associations	Clays are secondary minerals, often residual, formed by alternation of Al-rich silicates.	It is common rock-forming secondary mineral, forming after aluminous silicates, component of soils and replaces feldspar in rocks undergoing weathering. Associated mineral is quartz.

Table 2.9: Description of clay mineral group

	Pyrophyllite	*Talc*
Origin of name	From the Greek pyro and phyllon, meaning "fire" and "leaf", in reference to this mineral's behaviour when heated.	From the Arabic talq, meaning "pure".
Structure and composition	The three layered structure consists of individual sheets of $Al(O,OH)_6$ octahedra sandwiched between sheets of SiO_4 tetrahedra. Fe may replace some of Al: minor Mg, Ca and Na may be present.	Talc is isostructural with pyrophyllite, being composed of layers of SiO_4 tetrahedra. It may contain some Ti, Ni and Fe.
Habit	Individual crystals are unknown. It is usually massive and foliated, sometimes forming platy or radiating masses.	Rare tabular pseudohexagonal crystals have been found, but talc is usually very fine grained and massive.
Crystallography	Triclinic, $a = 5.16$, $b = 8.96$, $c = 9.35$, $\beta = 100.37°$, $\alpha = 90.03°$, $\gamma = 89.75°$, $Z = 2$	Monoclinic, $a = 5.29$, $b = 9.10$, $c = 18.81$, $\beta = 100.00°$, $Z = 4$

(*Contd.*)

Table 2.9 (*Contd.*)

Hand specimen identification	Greasy feel and cleavage help identify pyrophyllite, but it can't be told from other clays without X-ray data.	Greasy feel, massive habit, cleavage and association help identify talc.
Physical properties		
Colour	White	Grey, white
Streak	White	White
Transparency	Translucent	Translucent
Lustre	Pearly	Silky
Cleavage	Perfect basal (001)	Perfect basal (001)
Fracture	Not seen	Flexible
Hardness	1-2	1
Specific gravity	2.8	2-8
Optical properties	High birefringence, perfect cleavage, bird's-eye maple appearance and lack of colour identify pyrophyllite. Biaxial (-), $\beta = 1.588°$, $\alpha = 1.553°$, $\gamma = 1.600$, $\delta = 0.047$, $2V = 52°$-$62°$	Talc is similar to muscovite, chlorite and pyrophyllite, but has a smaller $2V$ and often appears smeared or poorly defined when viewed under crossed polars. Biaxial (-), $\beta = 1.58°$, $\alpha = 1.54°$, $\gamma = 1.58$, $\delta = 0.05$, $2V = 6°$-$30°$
Occurrence and associations	Pyrophyllite is found in low- and medium-grade metamorphosed shales. Associated minerals include kyanite, feldspar and quartz.	Talc is a primary mineral in some low-grade metamorphic rocks, including marbles and ultramafic rocks, and less commonly a secondary mineral in mafic igneous rocks.

Concluding Remarks

Industrial and environmental applications of a particular type of clay depend on its physical and chemical properties, which in turn are determined by its chemical composition and internal structure. This chapter prepares a background for such studies.

QUESTIONS

1. How will you distinguish the following minerals?
   (a) Kaolinite and montmorillonite
   (b) Talc and pyrophyllite

2. Differentiate between clay and clay mineral and explain elaborating the constituents and phases of clay.

FURTHER READING

Barshad, I. (1948). Vermiculite and its relation to biotite as revealed by base exchange reactions, X-ray analysis, differential thermal curves and water content. *Am. Mineral.*, **33:** 655-678.

Barshad, I. (1950). The effect of the interlayer cations on the expansion of the mica type crystal lattice. *Am. Mineral.*, **35:** 225-238.

Bradley, W.F. (1944). Diagnostic criteria for clay minerals. *Am. Mineral.*, **30:** 704-713.

Brown, G. and Macewan, D.N.C. (1950). The interpretation of x-ray diagrams of soil clays. Part II. *Jour. Soil Sci.*, **1:** 606-612.

Dextral Parkins (2002). Mineralogy (2nd edition). Prentice Hall of India Limited, New Delhi.

Ehlers, Ernest G. and Blatt, Harvey (1982). Petrology: Igneous, Sedimentary and Metamorphic. W.H. Freeman and Company, San Francisco.

Guggenheim, S. and Martin, R.T. (1995). Definition of clay and clay mineral: Joint Report of the AIPEA nomenclature and CMS nomenclature committees. *Clays and Clay Minerals*, **44(5):** 713-715.

Klein, C. and Hurlbut, C.S. (1993), Jr. Manual of Mineralogy (21st ed.). John Wiley and Sons, New York.

Kunze, G.W. (1952). Weathering of micas and their role in potash fixation. Ph.D. Thesis, Pennsylvania State College.

Mackenzie, R.C., Walker, C.F. and Hart, R. (1949). Ilite occurring in decomposed granite at Ballater, Aberdeenshire. *Mineral. Mag.*, **28:** 707-714.

Moore, D. and Reynolds, R.C. Jr. (1997). X-Ray Diffraction and the Identification and Analysis of Clay Minerals (2nd ed.). Oxford University Press, New York.

Mortland, N.M. and Gieseking, J.B. (1951). Influence of the silicate ion on potassium fixation. *Soil Science*, **71:** 381-385.

Philips, F.C. (1963). An Introduction to Crystallography (3rd ed.). John Wiley and Sons, New York.

Ross, C.S. and Hendricks, S.B. (1945). Minerals of the montmorillonite group. U.S. Geological Survey, Prof. Paper, 205-B, 27-79.

Weaver, C.E. and Bates, T.F. (1951). Mineralogy and petrology of the Ordovician K-bentonites and related limestones. *Geol. Soc. Am., Bull.*, **62:** 1438 (Abs.).

White, J.L. (1950). Transformation of illite into montmorillonite. *Soil Science Soc. of Am. Proc.*, **15:** 129-133.

CHAPTER

3

INTERNAL STRUCTURES OF CLAY MINERALS

In this chapter, we are going to explore the internal structure of the clay minerals, the minerals that impart plasticity to the clays and harden upon drying or firing. As stated in Chapter 1, all the clay minerals detected so far belong to phyllosilicate subclass of silicate class. All minerals belonging to a particular class have some chemical and physical similarities, and those having greater degree of compositional and/or structural resemblances among them are grouped together in a subclass. Therefore this chapter starts with a brief description of silicate class, followed by an explanation of the internal structure of phyllosilicate subclass. The succeeding sections describe the internal structures of the five clay mineral groups: kaolinite, illite, smectite, vermiculite and palygorskite.

3.1 INTRODUCTION

In geological terms, the term "clay" is ambiguous and has multiple meanings: a group of fine grained minerals i.e., the clay minerals; a particle size (smaller than silt); and a type of rock i.e., a sedimentary deposit of fine-grained material usually composed largely of clay minerals (Patterson and Murray, 1983; Bates and Jackson, 1987). Clay, one of the leading minerals, is a widely distributed, abundant mineral resource of major industrial importance for an enormous variety of uses (Ampian, 1985).

3.2 EFFECT OF TEMPERATURE VARIATION ON CATION EXCHANGE VARIATION

At high temperature and during very rapid growth of a crystal, the ions are randomly arranged in the structural framework of a substance. There is very little or no regular pattern in their arrangement. Such an arrangement gives

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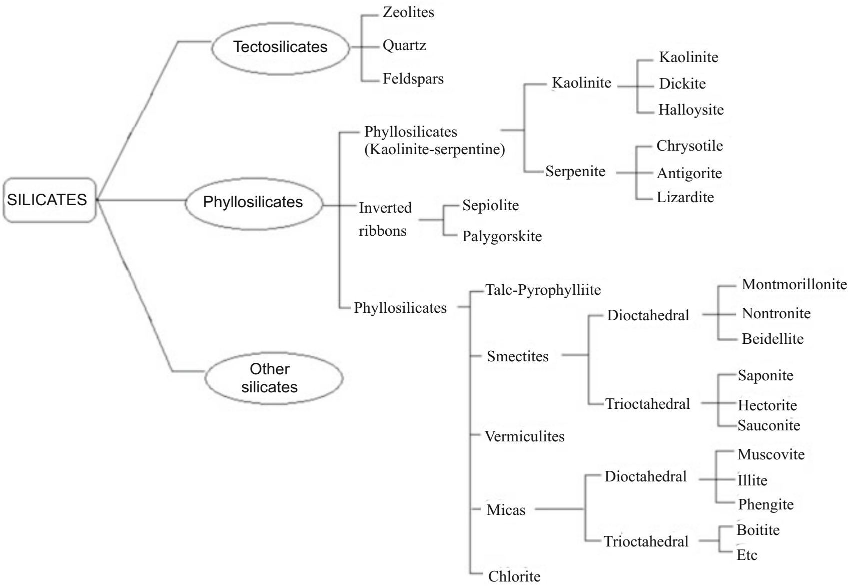

Fig. 3.1: Classification of silicates (Bailey, 1980b; Rieder et al., 1998).

rise to disordered structure. In this case one type of ions may occupy the sites specified for the others. Let us assume there are two types of cations in a substance, occupying two distinct cations in its structure. In a perfectly ordered state, one type of cation will only occupy a particular site, and never occupies the site specified for the other. So the probability of a particular site to be filled up by a particular cation is 100%.

In a totally disordered state, a particular site may be occupied by any of the two cations. So the probability of one particular site to be filled up by one particular cation is 50%.

In partially ordered (or disordered) or totally random, the probability of a particular site to be filled by a particular cation ranges from 50% to 100%, depending upon the degree of order (or disorder) in the structure.

There is no definite transition point between perfect order and total disorder. Perfect order is possible only at 0° K; with increase of temperature, disorder starts and the degree of order decreases. At high temperature just below the melting point, the structure tends to become completely disordered and ready to break away.

Example: In K-feldspar, Al^{+3} replaces Si^{+4} in the tetrahedral sites. In the high temperature from sanidine, Al^{+3} has a disordered distribution in the SiO_2 network. Microcline, the low temperature polymorph, shows an ordered distribution of the two cations. Orthoclase, which is crystallized in intermediate temperature, has a degree of order in between the other two polymorphs.

3.3 SILICATE CLASS

All minerals belonging to silicate class contain the dominant anionic group SiO_4^{-4}, where each Si^{+4} cation is surrounded by four O^{-2} anions. If the centres of the four O^{-2} are joined by imaginary lines, a tetrahedron is obtained with the Si^{+4} situated at its centre (Fig. 3.2). This SiO_4^{-4} tetrahedron is the basic structural unit of all silicate minerals. The Si–O bond is neither completely ionic nor completely covalent; it is said to be 50% ionic bond. The bond angle between each Si–O bond in the tetrahedron is 109.5°.

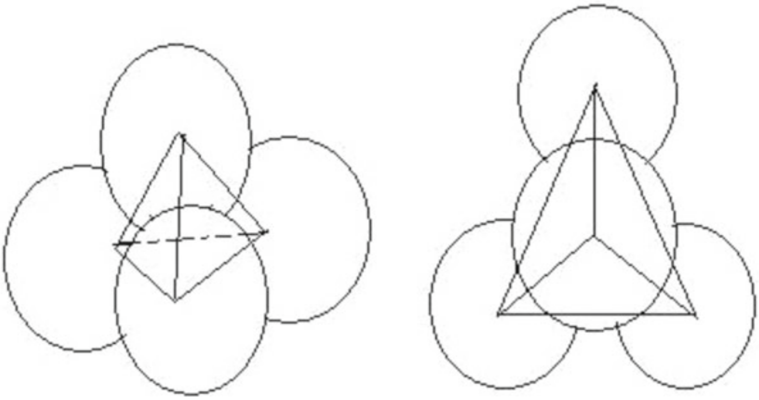

Fig. 3.2: The SiO_4^{-4} tetrahedron is constructed by joining the centres of four O^{-3}. The Si^{+4}, having ionic radius one-fifth of that of O^{-2}, is shown at the centre of tetrahedron behind the O^{-3}. *Left*: side view. *Right*: plan view.

In some silicate minerals, some of the tetrahedra may have Al^{+3} at their centres instead of Si^{+4}. This is commonly referred as substitution of Si^{+4} by Al^{+3}. It necessitates inclusion of some cation in the mineral structure, or substitution of a low-valency cation by a high-valency cation, for balancing the excess negative charge.

Each SiO_4^{-4} tetrahedron has an unbalanced charge of –4, which can be neutralized in the following two ways:

- **Bonding with cations:** An SiO_4^{-4} tetrahedral group can be bonded to cations. Generally bivalent cations like Mg^{+2}, Fe^{+2}, Ca^{+2} etc. are bonded to the tetrahedral group in common silicate minerals. The monovalent cations like Na^{+}, K^{+} and the trivalent cations like Fe^{+3}, Al^{+3} etc. are also common. These cations are generally surrounded by six O^{-2} to form an octahedral coordination site.

- **Linking of tetrahedra:** Two or more tetrahedra can be linked together by their apical oxygens. The O^{-2} that links two adjacent tetrahedra is known as *bridging oxygen,* and its charge is shared by two Si^{+4}. Since Si^{+4} is a highly charged cation, the centres of the adjacent tetrahedra should be separated as far as possible to make the structure stable.

> Therefore, when two SiO_4^{-4} tetrahedra are linked together, only one apical oxygen will be shared between them. If two adjacent tetrahedra are connected by two or three apical oxygens between them, sharing an edge or a face respectively, then their centres would be very close to each other and the structure would be unstable due to the strong repulsive force between the central Si^{+4} ions. Therefore an SiO_4^{-4} tetrahedron can share two apical oxygens with *two adjacent tetrahedra*, and not with *a single tetrahedron*. In other words, there can be *only one bridging oxygen* in between two adjacent tetrahedra. If one tetrahedron has 2, 3 or 4 bridging oxygens, then it must be linked to 2, 3 or 4 adjacent tetrahedra respectively.

Different arrangements of linking of apical oxygens give rise to the different silicate subclasses, as discussed here.

3.3.1 Subclass Nesosilicate

In this subclass, no apical oxygen of one SiO_4^{-4} tetrahedron is shared with other SiO_4^{-4} tetrahedra, i.e. no bridging oxygen in the tetrahedron. In this group the oxygens are shared with octahedral groups that contain other cations like Mg^{+2}, Fe^{+2}, or Ca^{+3}. Common examples are olivines, garnets, Al_2SiO_5 minerals (andalusite, kyanite and sillimanite), staurolite and sphene.

3.3.2 Subclass Sorosilicate

In this case, one of the apical oxygens of one tetrahedron is shared with another tetrahedron, i.e. one bridging oxygen in each tetrahedron (Fig. 3.3A). The basic structural unit is $Si_2O_7^{-6}$. Example: Hemimorphite - $Zn_4Si_2O_7(OH)\cdot H_2O$.

3.3.3 Subclass Cyclosilicate (Ring Silicates)

In cyclosilicates, two of the apical oxygens of each tetrahedron are shared with two adjacent tetrahedra, and the linked tetrahedra are arranged in a ring (Fig. 3.3B). The ring may be formed by linking of 3, 4, 5 or 6 tetrahedra, forming the structural units $Si_3O_9^{-6}$, $Si_4O_{12}^{-8}$, $Si_5O_{15}^{-10}$ and $Si_6O_{18}^{-12}$ respectively. In each case Si:O ratio is 1:3. Example: Beryl – $Be_3Al_2Si_6O_{18}$.

3.3.4 Subclass Inosilicate – Single Chain

In this structure two apical oxygens of each SiO_4 tetrahedron are shared in a way to form a long single chain of linked tetrahedra. (Fig. 3.3C). The basic structural unit of single chain inosilicates is $Si_2O_6^{-4}$ or SiO_3^{-2} with an Si:O ratio of 1:3. In some cases Al^{+3} can replace Si^{+4} in the tetrahedral site.

3.3.5 Subclass Inosilicate – Double Chain

In the double chain inosilicates, two parallel chains are linked together by their alternate tetrahedra. (Fig. 3.3D). The basic structural group is $Si_4O_{11}^{-6}$. The

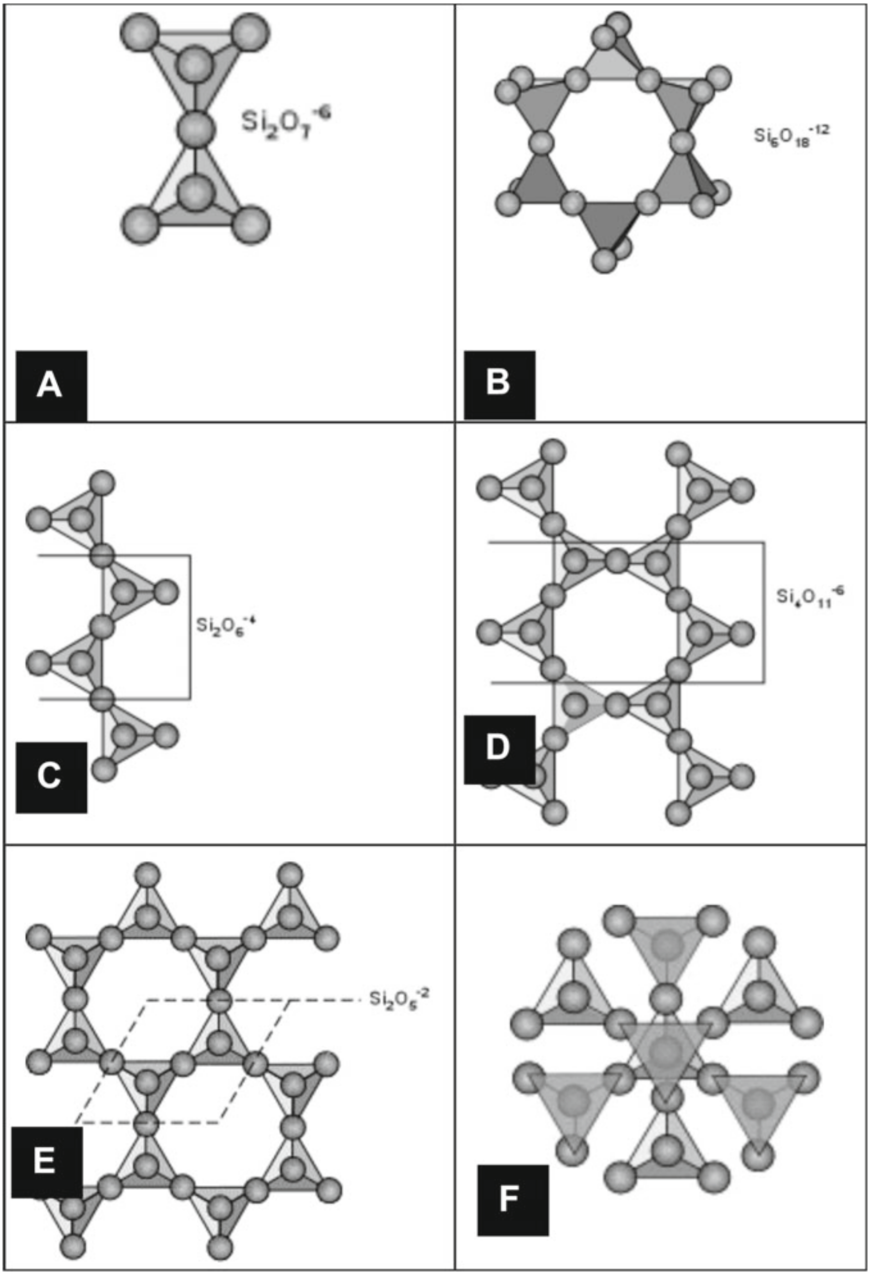

Fig. 3.3: Depending on their mutual bonding various types of SiO_4 tetrahedra are shown here.

amphibole group of minerals are double chain silicates, for example the tremolite-ferroactinolite series - $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_3$.

3.3.6 Subclass Phyllosilicates (Sheet Silicates)

In this structure each SiO_4 tetrahedron is linked to three adjacent tetrahedra to form an infinite sheet of tetrahedra (Fig. 3.3E). Each tetrahedron in the sheet thus shares three (out of four) apical oxygens, having the basic structural unit $Si_2O_5^{-3}$. The micas, clay minerals, chlorite, talc and serpentine minerals are examples of phyllosilicates.

3.3.7 Subclass Tectosilicates (Framework Silicates)

The tectosilicates or framework silicates have a structure where all of the four oxygens of an SiO_4^{-4} tetrahedron are shared with four adjacent tetrahedra (Fig. 3.3F). The ratios of Si to O is thus 1:3. The basic structural group then becomes SiO_3. The minerals quartz, cristobalite, tridymite etc. are based on this structure. If some of the Si^{+4} ions are replaced by Al^{+3}, a charge imbalance is produced which is neutralized by incorporation of other cations in different coordination sites within the framework structure. Thus, the feldspar and feldspathoid minerals are also based on the tectosilicate framework.

3.4 SUBCLASS PHYLLOSILICATE (LAYERED/SHEET SILICATE)

Most minerals belonging to this subclass have platy or flaky habit, and can be divided into thin, leaf-like parts for which they are called phyllosilicates (Greek *Phyllon* – leaf). Internally, each SiO_4^{-4} tetrahedron is linked to three neighbouring tetrahedra by sharing apical oxygens, *forming a layer or sheet of SiO_4^{-4} tetrahedra*. For this reason they are also called *layered* or *sheet* silicates.

Some general aspects of the internal structures of phyllosilicates are described below:

(i) In each SiO_4^{-4} tetrahedron, three apical oxygens are shared with three neighbouring tetrahedra. Therefore each tetrahedron has three bridging oxygens and one non-bridging oxygen. In a sheet of SiO_4^{-4} tetrahedra (known as the *t*-sheet), each non-bridging oxygen points towards the same direction.

(ii) Most phyllosilicates are hydroxyl-bearing. The OH^- group is located at the same plane of non-bridging oxygens of the *t*-sheet. It is surrounded by six non-bridging oxygens (Fig. 3.4).

(iii) In the *t*-sheet, each tetrahedron has a negative charge of –4. The OH- group provides additional negative charge to the structure. This excess negative charge is neutralised by the bivalent cations (Mg^{+2}, Fe^{+2} etc.) or trivalent cations (mainly Al^{+2}). Each cation is surrounded by six anions or anionic groups (O^{-2} or OH^- respectively). The O^{-2} are the non-bridging oxygens of the *t*-sheet, and the OH^- are the hydroxyl groups situated at the same plane. If the centres of the six O^{-2} or OH^- surrounding a cation are joined, a tilted octahedron is obtained (Fig. 3.5). These cations are therefore known as *octahedral cations* of phyllosilicate structures, and the O^{-2} or OH^- are called *apical anions.* Since the octahedra share the non-bridging oxygens of the *t*-sheet, they are attached to the *t*-sheet, the triangle obtained by joining two non-bridging O^{-2} and one OH^- forms one face of the octahedron.

(iv) **Trioctahedral and dioctahedral structures**: If the octahedral cations are bivalent, each apical anion of octahedron is surrounded by three cations. In that case all the octahedra attached to the *t*-sheet have bivalent cations in their centres.

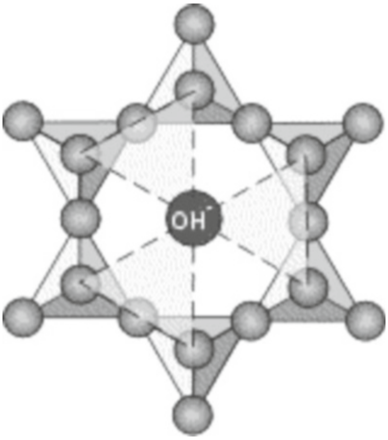

Fig. 3.4: Plan view of *t*-sheet showing position of OH^- group.

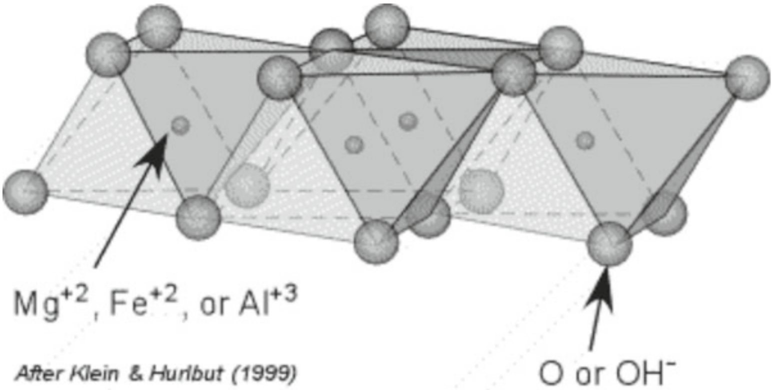

Fig. 3.5: Side view of the cation-centred octahedral.

On the other hand, if the octahedral cations are trivalent, each apical anion of octahedron is surrounded by two cations. In that case, two-third octahedra attached to the *t*-sheet have trivalent cations in their centres, and the remaining one-third are vacant.

(v) **Arrangement of tetrahedra and octahedra in phyllosilicates – the *o*-sheet**: The cation-centred octahedra may be linked together by sharing their apical anions to form an infinitely extended octahedral sheet, known as the *o*-sheet. The phyllosilicate subclass is divided into a number of structural types based on the arrangement of *t*-sheets and *o*-sheets, as described below.

***t-o* structures** (1:1 structure): One *t*-sheet is connected to one *o*-sheet, to form a *t-o* layer. These *t-o* layers are electrically neutral. They are bonded to one another by weak van der Waals bonds. Examples: Kaolinite (dioctahedral), antigorite, lhizardite (trioctahedral) etc. (Fig. 3.6).

***t-o-t* structures** (2:1 structure): One *o*-sheet is situated in between two *t*-sheets, to form a *t-o-t* layer. The non-bridging oxygens of the two *t*-sheets face each other, and the apical oxygens of both of them are shared by the octahedra of the intervening *o*-sheet. These *t-o-t* layers are electrically neutral. They are bonded to one another by weak van der Waals bonds. Examples: talc (trioctahedral), pyrophyllite (dioctahedral) (Fig. 3.7).

***t-o-t-c* structures:** If Si^{+4} is substituted by Al^{+3} in some of the tetrahedra, the net positive charge of a *t-o-t* layer decreases. The excess negative charge is balanced by inclusion of cations in between two *t-o-t* layers. These cations are known as interlayer cations. An interlayer cation is surrounded by 12 oxygens: six bridging oxygens from each *t-o-t* layer in its opposite sides. So its position is known as the 12-fold coordination site (Fig. 3.8).

If Si^{+4} is substituted by Al^{+3} in one-fourth of the tetrahedral sites, one monovalent cation in the 12-fold coordination site (like K^+, Na^+ etc.) can balance the excess negative charge. Example: illite, muscovite, paragonite (dioctahedral), biotite, phlogopite (trioctahedral) etc.

If Si^{+4} is substituted by Al^{+3} in half of the tetrahedral sites, one bivalent cation is required in the 12-fold coordination site (like Ca^{+2}) to balance the

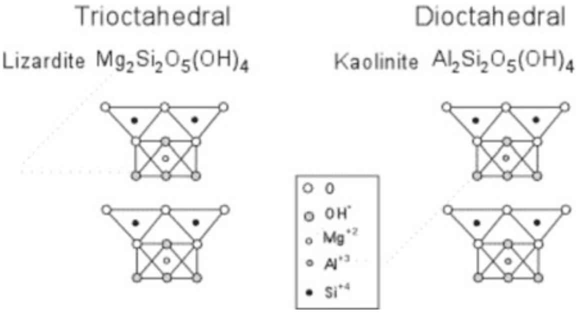

Fig. 3.6: *t-o* structures.

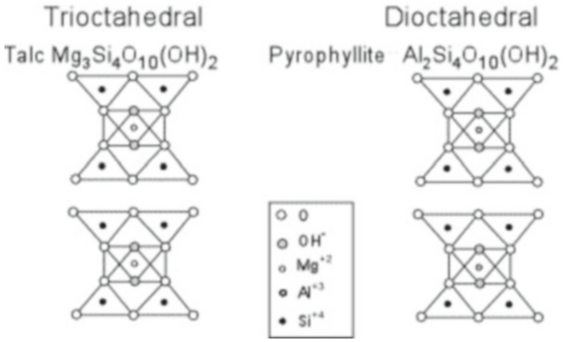

Fig. 3.7: *t-o-t* structures.

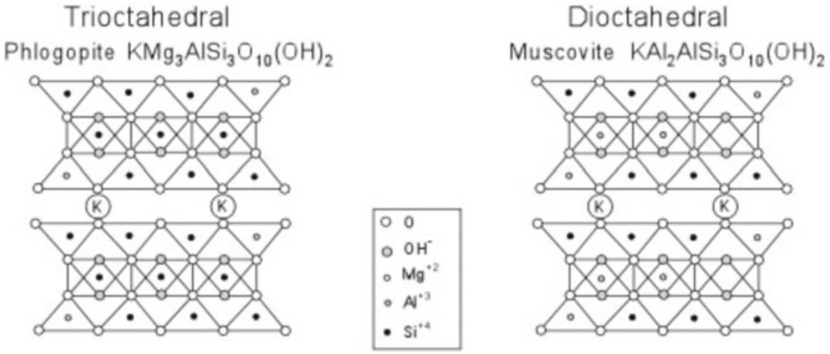

Fig. 3.8: *t-o-t-c* structures.

excess negative charge. Example: margarite (dioctahedral), clintoniote (trioctahedral) etc.

3.5 INTERNAL STRUCTURE OF KAOLINITE GROUP

The clay minerals of kaolinite group have dioctahedral *t-o* structure. This type of structure consists of three planes of anions. On one side, there is a plane of bridging O^{-2} of the *t*-sheet, on the other side there is a plane of OH^-. The middle anionic plane consists of the non-bridging oxygens of the *t*-sheets and OH^-. In the *o*-sheet, each octahedral cation is surrounded by three OH^- from the plane of OH^-, one OH^- and two non-bridging oxygens from the middle plane.

The *t-o* layers are electrically neutral, and bonded to one another by weak Van der Waals bond or hydrogen bond. The basal spacing (repeat distance from one layer to the next) is about 7 Å.

The general chemical formula of kaolinite is:

$$Al_2\,[Si_2O_5]\,(OH)_4$$

Halloysite has a characteristic property of absorbing water. The water molecules are arranged in a sheet in the interlayer space, i.e. in between two *t-o* layers. In that sheet, each H_2O is bonded to each other and also to tetrahedral oxygens by weak hydrogen bonding. On heating or drying, that bonding can be easily broken and the H_2O is expelled from the structure. In dehydrated condition, the basal spacing of halloysite is same to that of other kaolinites, i.e. 7 Å. But on absorbing water, the spacing between successive *t-o* layers increases by formation of the H_2O sheet in between them, increasing the basal spacing to a maximum of 10 Å.

3.6 INTERNAL STRUCTURE OF ILLITE GROUP

This group has trioctahedral or dioctahedral *t-o-t-c* structure, in which each *o*-sheet is sandwiched between two inward-pointing *t*-sheets. In the *o*-sheet, four out of six apical anions of each octahedron are O^{-2}, the remaining two are OH^-

The illite group minerals have a structure similar to that of muscovite, but there is less substitution of Si^{+4} by Al^{+3} in the tetrahedral sites. As a consequence, there are less interlayer cations and the illites are typically deficient in alkalies than muscovite. Thus, the general formula for the illites is:

$$K_yAl_4\,[(Si_{8-y},Al_y)O_{20}]\,(OH)_4$$

Usually $1 < y < 1.5$, but always $y < 3$.

Because of possible charge imbalance, Ca and Mg can also sometimes substitute for K.

The basal spacing of illite is 10 Å. The K, Ca or Mg interlayer cations prevent the entrance of H_2O into the structure. For this reason the basal spacing in illite is constant. Thus, the illite group minerals cannot expand by absorption of water like halloysite, vermiculite and smectite.

3.7 INTERNAL STRUCTURE OF SMECTITE GROUP

This group has trioctahedral or dioctahedral *t-o-t-c* structure, in which each *o*-sheet is sandwiched between two inward-pointing *t*-sheets. In the *o*-sheet, four out of six apical anions of each octahedron are O^{-2}, the remaining two are OH^-.

Both tetrahedral and octahedral cations are substituted by cations of lower charge. The charge imbalance thus produced is neutralised by a small number of interlayer cations like Ca^{+2} or Na^+, but they don't occupy all the available vacant sites between two *t-o-t* layers. They are probably arranged in alternating chains of occupied and vacant sites (Deer et al., 1992).

Most common clay mineral of this group is montmorillonite, the general chemical formula of which is given below:

$$(\tfrac{1}{2}Ca,Na)(Al,Mg,Fe)_4[(Si,Al)_8O_{20}](OH)_4\cdot nH_2O$$

It is to be noted here that it contains nH_2O, which must be differentiated from the OH^-. While the former occupies the interlayer spaces, the latter occurs in the plane of non-bridging oxygens of *t*-sheets. Smectites can readily absorb water, and the H_2O molecules are accommodated in the interlayer vacant spaces. They form hydration shells around the interlayer cations. Single or multiple sheets of H_2O can occupy the interlayer spaces. As the number of H_2O sheets increases, the basal spacing also increases, as given in Table 3.1.

Table 3.1: Relation between number of H_2O sheets and basal spacing

Number of H_2O sheets (in between two t-o-t layers)	*Basal spacing (Å)*
Nil (Fully collapsed state)	9.6
1	13.5
2	15.5
3	19.0

As the basal spacing increases, the structure expands. Smectites thus expand on absorption of water. On heating between 100-200°C, much of the interlayer H_2O is lost, and basal spacing decreases to about 10 Å. When heated above 500°C, basal spacing reduces further to 9.6 Å and the structure comes to fully collapsed state.

3.8 INTERNAL STRUCTURE OF VERMICULITE GROUP

This group has trioctahedral or dioctahedral *t-o-t-c* structure, in which each *o*-sheet is sandwiched between two inward-pointing *t*-sheets. In the *o*-sheet, four out of six apical anions of each octahedron are O^{-2}, the remaining two are OH^-.

Substitution of Si^{+4} by Al^{+3} in the tetrahedral site causes excess negative charge, which is balanced by interlayer cations. The most common interlayer cation in vermiculites is Mg^{+2}; others are Ca^{+2} and Na^+.

Vermiculites can readily absorb water, and in the maximum hydrated state the H_2O molecules occur along two sheets in the interlayer space. In such a H_2O sheet, each H_2O molecule has hydrogen bond with the neighbouring one, which weakly bound them together. There is also hydrogen bond in between the H_2O and neighbouring O^{-2} of the *t-o-t* layer. The two pairs of H_2O sheets are held together by the Mg^{+2}, which lies midway between them.

The general chemical formula of vermiculites is given below:

$$(Mg,Ca,Na)_{0.6-0.9}(Mg, Fe^{+3}, Al)_6[(Si,Al)_8O_{20}](OH)_4 \cdot nH_2O$$

At high temperature and low humidity, vermiculite loses some of the interlayer H_2O, and there is only one H_2O sheet in the interlayer space. When temperature is higher, all the H_2O molecules may be expelled, giving rise to fully collapsed structure.

The basal spacing in vermiculite depends on the number of H_2O sheets in the interlayer space, as shown in Table 3.2.

Table 3.2: Relation between number of H_2O sheets and basal spacing

Number of H_2O sheets (in between two t-o-t layers)	*Basal spacing (Å)*
Nil (Fully collapsed state)	9.0
1	11.7
2	14.3

3.9 INTERNAL STRUCTURE OF PALYGORSKITE-SEPIOLITE GROUP

They are finely fibrous minerals; still they have many structural similarities with the other clay minerals. They have *t*-sheets like the other phyllosilicates, but the cationic octahedra are linked together to form chains or ribbons, not the *o*-sheets like other phyllosilicates. These octahedral chains are attached to the *t*-sheets, with much vacant spaces left in between them. Those vacant channels can accommodate water molecules and also organic molecules.

Concluding Remarks

This chapter deals about the internal structure of the clay minerals, which determines their response to the physical and chemical changes. The chemical and thermodynamic aspects which control the formation process will be discussed in the next chapter, and the physical properties are presented in Chapter 5.

QUESTIONS

1. The variation of anionic groups controls the mineral characters. Elaborate with examples.
2. Explain the different type of atomic packing to construct crystals of various morphologies.
3. Crystal property has an impact on physical properties of minerals; explain with suitable examples.
4. Sharing of apical oxygen and linking of SiO_4 tetrahedra form different silicate subclasses. Explain it with neat sketches.

FURTHER READING

Blackburn, W.H. and Dennen, W.H. (1994). Principles of Mineralogy (2nd ed.). William C. Brown, Dubuque, IA.

Bloss, F.D. (1994). Crystallography and Crystal Chemistry: An Introduction. Mineralogical Society of America, New York.

Deer, W.A., Howie, R.A. and Zussman, J. (1962). Rock Forming Minerals (5 vols.). John Wiley and Sons, New York.

Deer, W.A., Howie, R.A. and Zussman, J. (1992). An introduction to the rock-forming minerals (2nd ed.). Longman, London. ISBN 0-582-30094-0.

Deer, W.A., Howie, R.A., Wise, W.S. and Zussman, J. (2004). Rock-forming minerals. Volume 4B. Framework silicates: Silica minerals, feldspathoids and the zeolites (2nd ed.). Geological Society of London, London.

Ehlers, Ernest G. and Blatt, Harvey (1982). Petrology: Igneous, Sedimentary and Metamorphic. W.H. Freeman and Company, San Francisco.

Guggenheim, Stephen and Martin, R.T. (1995). Definition of clay and clay mineral: Join report of the AIPEA nomenclature and CMS nomenclature committees. *Clays and Clay Minerals*, **44(5):** 713-715.

Hurlbut, Cornelius S. (1966). Dana's Manual of Mineralogy (17th ed.). ISBN 0-471-03288-3.

Hurlbut, Cornelius S. and Klein, Cornelis (1985). Manual of Mineralogy (20th ed.). Wiley. ISBN 0-471-80580-7.

Klein, C. and Hurlbut, C.S. (1993). Jr. Manual of Mineralogy (21st ed.). John Wiley and Sons, New York.

Kunze, G.W. (1952). Weathering of micas and their role in potash fixation. Ph.D. Thesis, Pennsylvania State College.

Mackenzie, R.C., Walker, C.F. and Hart, R. (1949). Ilite occurring in decomposed granite at Ballater, Aberdeenshire. *Mineral. Mag.*, **28:** 707-714.

Moore, D. and Reynolds, R.C. Jr. (1997). X-Ray Diffraction and the Identification and Analysis of Clay Minerals (2nd ed.). Oxford University Press, New York.

Mortland, N.M. and Gieseking, J.B. (1951). Influence of the silicate ion on potassium fixation. *Soil Science*, **71:** 381-385.

Philips, F.C. (1963). An Introduction to Crystallography (3rd ed.). John Wiley and Sons, New York.

Skinner, H.C.W. (2005). Biominerals. *Mineralogical Magazine*, **69(5):** 621-641.

Wenk, Hans-Rudolf and Bulakh Andrei (2006). Minerals. Cambridge University.

CHAPTER

4

CHEMICAL PROPERTIES OF CLAY AND THERMODYNAMIC ASPECTS

Thermodynamic aspects which have effects on physical and chemical properties of clay minerals are discussed here.

4.1 INTRODUCTION

Chemical properties of clays are very important to the understanding of their behaviour. The electrical charge and colloidal size of clay mineral particles make them hydrate and interact so that their hydraulic conductivity and stress/strain properties are quite different from those of sandy soil. Thermodynamics describes how systems change when they interact with each other and also with their surroundings. During the above mentioned interactions, how the energy transfer is controlled by the thermodynamic parameters, is to be studied here.

It is always desirable to define a physico-chemical problem involving only equilibrium states in precise thermodynamic terms. The point of view may be sterile from the standpoint of suggesting fundamental, i.e. atomistic, interpretations of the experiments, but it has the great advantage of organizing the experimental results that immediately clarify at what points theoretical help is needed for further progress. The study of ion exchange on the clay minerals affords an excellent illustration of the advantages of the thermodynamic approach. Certainly the detailed effects observed in the experiments are of great complexity, and no simple interpretations can adequately account for them.

The clay properties to be discussed here are: (i) Clay mineral-water interaction, (ii) Gas penetrability, (iii) Hydraulic conductivity and (iv) Ion diffusivity, the details of which are listed in Table 4.1.

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Table 4.1a: Chemical properties of clay

Properties	
Clay mineral-water interaction	It is considered that clay-water interactions occurred from two different perspectives. First, the influence of the clay surface on the structure and properties of water will be examined. Most of the work on clay-water interactions has focused on this topic and has been the subject of several reviews (e.g. Sposito and Prost, 1982). Second, recent studies have demonstrated that the clay structure itself is influenced by changes in water content. Also, appropriate experimental methods have to be selected to provide information about the exchangeable cation itself.
Gas penetrability	In practice one can assume gas conductivity to be about a thousand times higher than that of water. Once gas has made its way through buffer clay and further out through even more permeable geological units, its rate of flow is more dependent on the availability of pressurized gas than on the gas conductivity. The factor "critical gas pressure" is the pressure which yields penetration through the buffer clay. According to current hypotheses micro-structural heterogeneity has a decisive influence on the critical gas pressure.
Hydraulic conductivity	Hydraulic conductivity is directly affected by bulk density and swelling pressure. High density and low electrolyte content of the clay mineral give rise to a very low conductivity for Na^+-smectite. On the other hand, the conductivity of Ca^{2+}-smectite is slightly higher because of its low densities. Hydraulic conductivity is depended on density at fluid saturation for different clay minerals. If the hydraulic gradient is high, the particles can also move and this affects the hydraulic conductivity. Thus, particle sand aggregates, that are set free, can be transported by flowing pore water to narrow parts of the pore spaces and cause clogging (Hansbo, 1960).
Ion diffusivity	The transport rate of dissolved ions and molecules in clays depends on their diffusivity under the influence of concentration gradients. Diffusion transport capacity is expressed by the "effective" diffusion coefficient. It refers to the actual "effective" porosity. On the other hand, the "apparent" diffusion coefficient derives directly from recording of the concentration profile in the clay. Thus, the importance of porosity is emphasised by the fact that cation diffusion takes place in several ways: in continuous water-filled voids, along particle surfaces with electrical double-layers, and through the interlayer space in smectites. The density of the clay plays a rather important role in ion diffusion except for clays exchanged with monovalent cations.

Table 4.1b: Cation-exchange capacity and specific surface area of minerals

Specific mineral data	*Cation-exchange capacity at pH 7 (milliequivalents per 100 grams)*	*Specific surface area (square metre per gram)*
Illite	10-40	10-100
Chlorite	10-40	10-55
Vermiculite	100-150	760
Kaolinite	3-15	5-40
Halloysite	40-50	1,100
Smectite	80-120	40-800
Allophane	30-135	2,200
Palygorskite-Sepiolite	3-20	40-180
Imogolite	20-30	1,540

4.2 THERMODYNAMIC SYSTEM

Thermodynamics is the subject of the relation of heat to forces acting between contiguous parts of bodies, and the relation of heat to electrical agency. It interrelates temperature, volume and pressure, which describe physical properties of material bodies, which are known as thermodynamic systems. Thermodynamics is built on the study of energy transfers that can be strictly resolved into two distinct components, heat and work.

A thermodynamic system is separated from the remainder of the universe by a boundary and everything outside this boundary is known as the surrounding. Exchanges of work, heat, or matter between the system and the surroundings take place across this boundary. The systems are categorized as open, closed and isolated depending on the types of interactions involved.

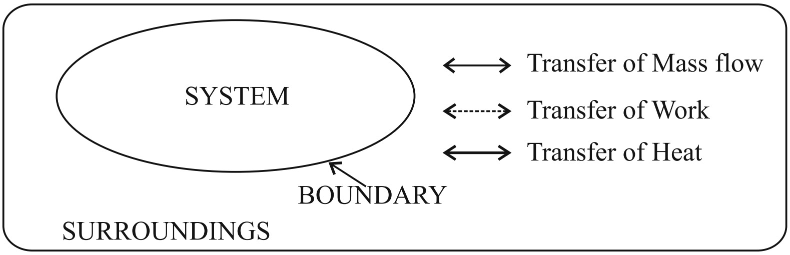
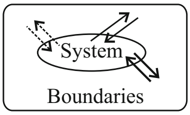
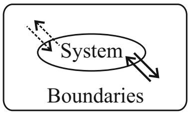
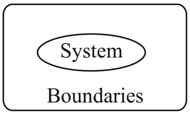


Fig. 4.1: Thermodynamic system.

The systems are categorized as open, closed and isolated depending on the types of interactions involved as shown in Table 4.2.

Table 4.2: Interactions of thermodynamic systems

Type of system depending on transfer of	Open 	Closed 	Isolated 
Mass flow	Yes	No	No
Work	Yes	Yes	No
Heat	Yes	Yes	No

Note: See Fig. 4.1 for legends.

4.3 THE PARAMETERS DESCRIBING THERMODYNAMICS

Entropy: It is considered in the second law of thermodynamics. It is thermodynamic property that can be used to determine the energy available for useful work in a thermodynamic process, such as in energy conversion devices, engines, or machines. In thermodynamics, the concept of entropy is defined by the second law of thermodynamics, which states that the entropy of an isolated system always increases or remains constant. Thus, entropy is also a measure of the tendency of a process, such as a chemical reaction, Thermodynamic entropy has the dimension of energy divided by temperature, and a unit of joules per kelvin (J/K) in the International System of Units.

Example:

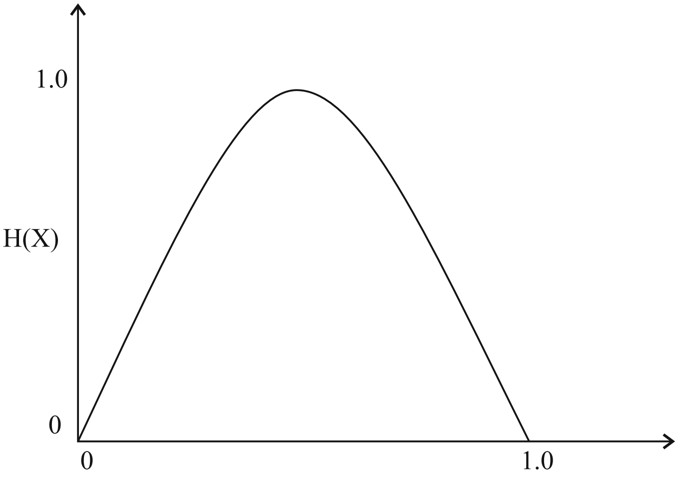


Fig. 4.2: Entropy $H(X)$ (i.e. the expected surprisal) of a coin flip, measured in bits, graphed versus the fairness of the coin $\Pr(X = 1)$, where $X = 1$ represents a result of heads.

Enthalpy: It is a thermodynamic potential. Enthalpy is a measure of the total energy of a thermodynamic system. It includes the internal energy. The total enthalpy, H, of a system cannot be measured directly. Thus, change in enthalpy, ΔH, is a more useful quantity than its absolute value. The change ΔH is positive in endothermic reactions, and negative in exothermic processes. The unit of measurement for enthalpy in the International System of Units (SI) is the joule, but other historical, conventional units are still in use, such as the British thermal unit and the calorie.

The First Law of thermodynamics for reversible processes:

$$dU = TdS - pdV$$

Apply the product for differentiation to pV:

$$dU = TdS + Vdp - d(pV),$$

Hence $$d(U + pV) = TdS + Vdp$$

The enthalpy of a system is defined as: $H = U + Pv$

So, $$dH(S,p) = TdS + Vdp$$

where H is the enthalpy of the system, U – the internal energy of the system, p – the pressure at the boundary of the system and its environment, V – the volume of the system, T – is absolute temperature and S is entropy.

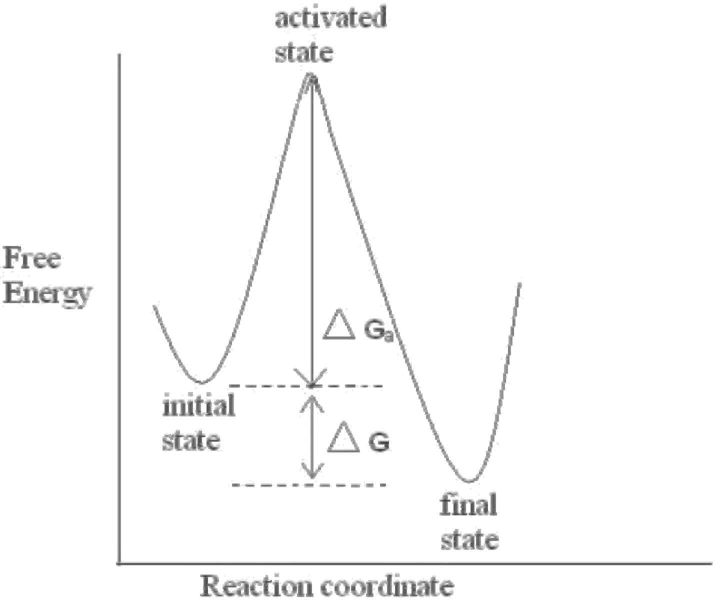


Fig. 4.3: The enthalpy changes due to transformation from initial state to final state.

Gibbs free energy: Gibbs free energy is a thermodynamic property that was defined in 1876 by the American mathematician Josiah Willard Gibbs to predict whether a process will occur spontaneously at constant temperature and pressure. Changes in the Gibbs free energy G correspond to changes in free energy for processes at constant temperature and pressure. ΔG is negative for spontaneous processes, positive for non-spontaneous processes and zero for processes at equilibrium. When a system changes from a well-defined initial state to a well-defined final state, the Gibbs free energy ΔG equals the work exchanged by the system with its surroundings, minus the work of the pressure forces, during a reversible transformation of the system from the same initial state to the same final state.

Gibbs free energy G is defined as

$$G = H - TS$$

where G is Gibbs free energy, H – enthalpy, S – entropy and T is temperature.

Assume, for example, that we start with the following reaction under standard-state conditions, as shown below.

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$$

The value of ΔG at that moment in time will be equal to the standard-state free energy for this reaction, ΔGo.

when $$Q\text{p} = 1: \Delta G = \Delta G\text{o}$$

As the reaction gradually shifts to the right, converting N_2 and H_2 into NH_3, the value of ΔG for the reaction will decrease. If we could find some way to harness the tendency of this reaction to come to equilibrium, we could get the reaction to do work. The free energy of a reaction at any moment in time is therefore said to be a measure of the energy available to do work.

When a reaction leaves the standard state because of a change in the ratio of the concentrations of the products to the reactants, we have to describe the system in terms of non-standard-state free energies of reaction. The difference between ΔGo and ΔG for a reaction is important. There is only one value of ΔGo for a reaction at a given temperature, but there are an infinite number of possible values of ΔG.

Concluding Remarks

This chapter presents an overview of thermodynamics and reaction kinetics of clay minerals to prepare a background for understanding their processes of formation in nature.

QUESTIONS

1. Interaction between various thermodynamic systems depends on transformation of some factors; explain with sketches.
2. Entropy, enthalpy and Gibbs free energy: how these terms are related with thermodynamics.

FURTHER READING

Blackburn, W.H. and Dennen, W.H. (1994). Principles of Mineralogy (2nd ed.). William C. Brown, Dubuque, IA.

Bloss, F. Donald (1971). Crystallography and Crystal Chemistry – An Introduction. Holt, Rinehart and Winston, New York.

Bridgman, P.W. (1943). The Nature of Thermodynamics. Harvard University Press, Cambridge MA.

Chatterjee, N.D. (1991). Applied Mineralogical Thermodynamics. Springer-Verlag, Heidelberg. en.wikipedia.org/wiki/Gibbs_free_energy.

Clark, John O.E. (2004). The Essential Dictionary of Science. Barnes & Noble Books. ISBN 0-7607-4616-8. OCLC 63473130 58732844 63473130.

Clausius, Rudolf (1850). On the Motive Power of Heat, and on the Laws which can be deduced from it for the Theory of Heat. Poggendorff's Annalen der Physik.

Crawford, F.H. (1963). Heat, Thermodynamics and Statistical Physics. Rupert Hart-Davis, London, Harcourt, Brace & World, Inc.

Deer, W.A., Howie, R.A. and Zussman, J. (1962). Rock Forming Minerals (5 vols.). John Wiley and Sons, New York.

Dixon, D.W. (1983). Radiation hazards to collectors of geological specimens containing natural radioactivity. National Radiological Protection Board Report 131 (UK).

Dugdale, J.S. (1998). Entropy and its Physical Meaning. Taylor and Francis. ISBN 0-7484-0569-0. OCLC 36457809.

Enrico Fermi (1956). Thermodynamics. Courier Dover Publications. ISBN 0-486-60361-X. OCLC 54033021 230763036 54033021.

Gibbs, Willard J. (1876). Transactions of the Connecticut Academy, III, Oct. 1875-May 1876 and May 1877-July 1878.

Guggenheim, E.A. (1933). Modern Thermodynamics by the Methods of J.W. Gibbs. Methuen, London.

Haase, R. (1963/1969). Thermodynamics of Irreversible Processes (translated in English). Addison-Wesley, Reading MA.

Haynie, Donald, T. (2001). Biological Thermodynamics. Cambridge University Press. ISBN 0-521-79549-4. OCLC 43993556.

Henderson, Paul (1982). Inorganic Geochemistry. Pergamon, New York.

Ilya Prigogine, I. and Defay, R. (Translated by D.H. Everett) (1954). Chemical Thermodynamics. Longmans, Green & Co., London.

Klein, C. and Hurlbut, C.S. (1993). Manual of Mineralogy (21st ed.). John Wiley and Sons, New York.

Kondepudi, D. (2008). Introduction to Modern Thermodynamics. Wiley, Chichester.

Lewis, G.N. and Randall, M. (1961). Thermodynamics (2nd ed.). Revised by K.S. Pitzer and L. Brewer. McGraw-Hill, New York.

Lewis, Gilbert N. and Randall, Merle (1923). Thermodynamics and the Free Energy of Chemical Substances. McGraw-Hill Book Co. Inc.

Nassau, K. (1978). The origin of color in minerals. *American Mineralogist*, **63:** 219-229.

Pauling, Linus (1960). The Nature of the Chemical Bond (3rd ed.). Cornell Univ. Press, Ithaca, NY.

Perkins, D. (2002). Mineralogy (2nd ed.). Prentice Hall of India.

Putnis, Andrew (1992). Thermodynamics: Introduction to mineral science. University of the Cambridge Publisher.

Reif, F. (1965). Fundamentals of Statistical and Thermal Physics. McGraw-Hill Book Company, New York.

Serrin, J. (1986). An Outline of Thermodynamical Structure. *In:* New Perspectives in Thermodynamics, J. Serrin (ed.). Springer, Berlin. ISBN 3-540-15931-2.

Smith, J.M., Van Ness, H.C. and Abbott, M.M. (2005). Introduction to Chemical Engineering Thermodynamics. McGraw Hill. ISBN 0-07-310445-0. OCLC 56491111.

Smyth, J.R. and Bish, D.L. (1988). Crystal Structures and Cation Sites of the Rock Forming Minerals. Allen and Unwin, London.

Thomson, Sir William (1882). Mathematical and Physical Papers, 1. C.J. Clay, M.A. & Son, Cambridge University Press, London.

Turner, L.A. (1962). Simplification of Carathéodory's treatment of thermodynamics. *Am. J. Phys.*, **30:** 781-786.

Wallace, J.M. and Hobbs, P.V. (2006). Atmospheric Science: An Introductory Survey (2nd ed.). Elsevier, Amsterdam. ISBN 978-0-12-732951-2.

Ziegler, H. (1983). An Introduction to Thermomechanics. North-Holland, Amsterdam.

Zussman, J. (1977). Physical Methods in Determinative Mineralogy. Academic Press, New York.

CHAPTER

5

PHYSICAL PROPERTIES OF CLAY AND SOIL MECHANICS

In this chapter genesis of soil and distinction with clay are discussed. Soil mechanics and related properties are also elaborated.

5.1 PHYSICAL PROPERTIES

Clay mineral particles are commonly too small for measuring precise optical properties. Specific gravity of most clay minerals are within the range from 2 to 3.3. Their hardness generally falls below 2.5. Refractive indices of clay

Table 5.1: Description of minerals

Name of minerals	*Size, shape and form of natural occurrences*
Keolinite	Well formed, six-sided flakes, with a prominent elongation in one direction.
Halloysite	Tubular units with an outside diameter ranging from 0.04 to 0.15 micrometre.
Smectite	Undulating mosaic sheets.
Illite	Poorly defined flakes commonly grouped together in irregular aggregates.
Chrysotile	Slender tube-shaped fibres having an outer diameter of 100–300 Å. Their lengths commonly reach several micrometres.
Palygorskite	Elongated laths, singly or in bundles. Frequently the individual laths are many micrometres in length and 50 to 100 Å in width.
Sepolite	Similar lath-shaped units.
Allophane	Very small spherical particles (30–50 Å in diameter), individually or in aggregated forms.
Imogolite	Long (several micrometres in length) thread-like tubes.

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minerals generally fall within a relatively narrow range from 1.47 to 1.68. Generally the size and shape, the two properties, are determined by electron micrographs.

It is important to note that physical properties depend on various other factors controlling the behavioural pattern of the material. Clay sedimentation properties depend on porosity, water content and minerals content of different specific gravity. Electrical conductivity depends on porosity, saturation, pore fluid conductivity, water content, and clay content. Velocity is very sensitive to saturation (air-water) but hardly at all to fluid composition. On the other hand, conductivity is very sensitive to both saturation and pore fluid conductivity. If saturation is determined from velocity, the fluid type can be determined uniquely from conductivity.

5.2 SOIL

The upper layer of Earth, which contains weathered rock materials, organic matter, humus-mineral mixture, glacial deposits, loam, silt, brown clay materials etc. in varying proportion, is known as soil. Depending on these constituents colour varies from black to dark brown. Formation of vegetation also depends on the presence of constituent materials.

Table 5.2: Types of soil and relevant terms

Soil	Residual soil: Soil that remains at the place of formation by chemical or physical weathering and eventually covers the parent rock is called residual soil. Transported soil: These soils are weathered materials, taken away at other places by the process of transportation, by several agents.
Sediments	Sediment is naturally occurring from process of weathering and erosion of existing rocks and subsequently by transportation process by fluid and wind, having large variation in size from boulder to colloidal.
Dirt	When plants and other things die, bugs, worms and other animals help to break the plants into little bits. Dirt is black and dark with lots of plants in it. When rock stay outside in sun and wind for long time, they start to disintegrate into small pieces until they become little tiny grains.
Sand	A loose granular substance, naturally occurring, typically pale yellowish brown composed of finely divided rock and mineral particles, resulting from the erosion of siliceous and other rocks and forming a major constituent of seabed, riverbed, etc. The composition of sand is highly variable, but the most common constituent of sand is silicon dioxide, or SiO_2, usually in the form of quartz.

Soil is a natural body having variable thicknesses. Soil differs from the parent materials in their morphological, physical and chemical characteristics due to interactions between the lithosphere, hydrosphere, atmosphere and biosphere. It is a mixture of mineral and organic constituents that are in solid, gaseous and aqueous states. In soil, particles are packed loosely, forming a soil structure filled with pore spaces. These pores contain soil solution (liquid) and air (gas).

Depending upon the nature of transporting agents, the transported soil may be of types described in Table 5.3.

Table 5.3: Types of soil depending on transporting agent

Type	*Definition*
Aeolian	Soil is transported by the action of wind.
Alluvial	Soil is transported by the water action.
Glacial	Soil is transported to the area through glaciers.
Colluvial	Soil is transported by gravity.

5.3 SOIL FORMATION

Soil formation process is known as pedognesis; it is the combined effect of physical, chemical and biological processes on soil parent material. In soil profile, soil horizons are formed from soil formation and this process involves additions, losses, transformation and translocation of material that compose soil. The formation of soil happens over a very long period of time. Due to process of weathering the surface rocks breakdown into smaller pieces and then mix with moss and organic matter. With progressing it creates a thin layer of soil. The plants attract animals, and when the animals die, their bodies decay. Decaying matter makes the soil thick and rich. Plants have a vital role for development of soil. Due to weathering process minerals are derived from weathered rocks which undergo changes that cause the formation of secondary minerals. These materials are variably soluble in water and so by this solving process these constituents are translocated from one area to another by water factor or animal activity. These movements and alteration are reasons of formation of different soil horizons.

In soil the most widespread mineral is quartz, feldspar and mica flakes though calcite and gypsum are present occasionally. Also there are important accumulations of kaolinite, zeolite and montmorillonite etc. Characterization of soil indicates its mechanical composition, i.e., the size of grains in it. The size of particles determines the various names of soil; thus there are stony, silty, sandy soils. In soil, organic matter is usually represented by humus, which consists of stable humic degradation matter, and their type depends on the plants from which it forms. Due to presence of humus in soil, various tint of grey, brown and black colours are attributed. Type and quantity of humus may be different depending on the natural conditions in which soil forms. Decomposition of plants and micro-organism forms humus. Due to the process of decomposition, organic matter lose their original shape. Cellulose and albumins are first to decompose. Lignite resists decomposition longer. Sometimes mineral part of plant tissues is preserved in humus.

Ground water plays an important role in soil, dissolving nutrient substances and thus these substances are absorbed by roots of plants. This solution contains large quantities of various salts and organic materials. Decomposition of organic matter which takes place in soil has complex reactions. These reactions increase the CO_2 content and release gases not contained in atmosphere. Soil air has less oxygen than atmospheric air. Soils largely consist of microorganism; there are tens of millions in one gram of soil. Composition of soil is influenced by climatic factors. Soil undergoes very great changes as a result of man's activity in cultivating and ploughing.

5.4 SOIL HORIZONS

The name of soil horizon is based on soil materials which reflect the specific process of soil formation. There are six horizons, named as with increasing depth: O horizon, A horizon, E horizon, B horizon, C horizon and R horizon. They are described and classified by their colour, size, texture, structure, pH, consistency, root quantity etc. Soil is consisting of O horizon, A horizon, E horizon and B horizon. Regolith is consisting of O horizon, A horizon, E horizon, B horizon and C horizon and bedrock consists of only R horizon.

Table 5.4: Types of horizon

Name of horizon	*Constituents*	*Description*
O horizon	High percentage of organic matter	The "O" stands for organic. It is a surface layer, dominated by the presence of large amounts of organic material in varying stages of decomposition. The O horizon contains no weathered mineral particles and is not part of the soil itself. O horizons may be divided into O1 and O2 categories, whereby O1 horizons contain decomposed matter whose origin can be spotted on sight and O2 horizons containing only well-decomposed organic matter, the origin of which is not readily visible.
A horizon	Humus-mineral mixture	The A horizon is the top layer of the soil horizons, consists of dark decomposed organic materials, which is called "humus". In this zone biological activity occurs. Soil organisms such as

(*Contd.*)

Table 5.4: (*Contd.*)

Name of horizon	*Constituents*	*Description*
		earthworms, arthopods, nematodes, fungi and many species of bacteria are concentrated in this zone. Thus the A horizon may be referred to as the biomantle. The soil biomantle is the organic-rich bioturbated topsoil where most biota lives, reproduce, die and become assimilated. So it is predominantly a product of organic activity, where bioturbation is a dominant process.
E horizon	Composed of silicates, stone layer	The horizon that has been significantly leached of its mineral and/or organic content, leaving a pale layer largely composed of silicates. These are present only in older, well-developed soils, and generally occur between the A and B horizons. In soils that contain gravels, due to animal bioturbation and stonelayer commonly forms near or at the base of the E horizon.
B horizon	Loam, silt, brown clay	The B horizon is commonly referred to as “subsoil”, consists of mineral layers which may contain concentrations of clay or minerals such as iron or aluminium oxides. This layer is also known as the “zone of accumulation”. Plant roots penetrate through this layer, but it has very little humus. It is usually brownish or red because of the clay and iron oxides washed down from A horizon. The B horizon may be divided into B1, B2 and B3 types. B1 is a transitional horizon to an A3 containing some A-horizon characteristics. B2 horizons have a concentration of clay, minerals, or organic debris. B3 horizons are transitional between the overlying B layers and materials of whether C or D horizons beneath it.
C horizon	Glacial deposits	This layer is little affected by soil forming processes. The C horizon may contain lumps or more likely large shelves of unweathered rock, The C horizon also contains parent material.
R horizon	Bed rock	R horizons basically denote the layer of partially weathered bedrock at the base of the soil profile. Unlike the above layers, R horizons largely comprise continuous masses of hard rock. Soils formed in situ will exhibit strong similarities to this bedrock.

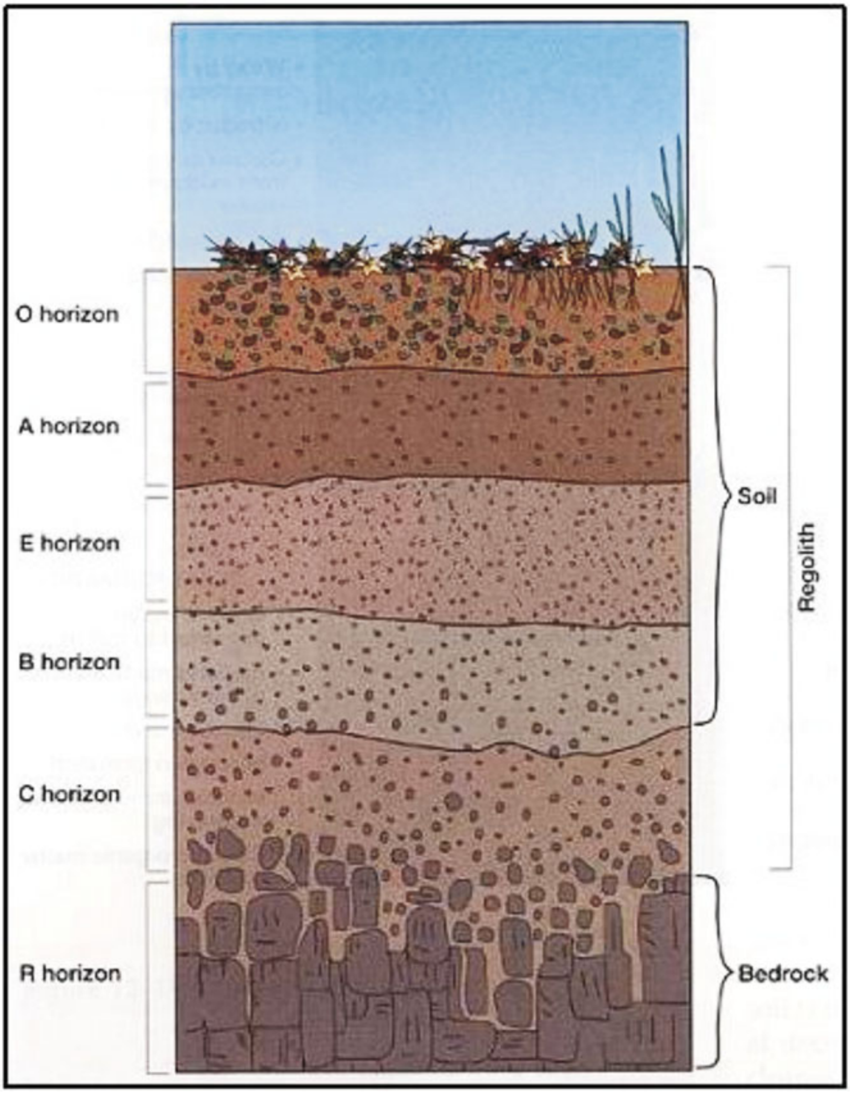
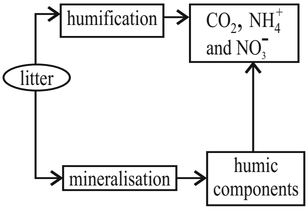


Fig. 5.1: Diagram of soil horizons.

5.5 SOIL GENESIS

The primary mechanism of soil creation is the weathering of rock. All types of rock (igneous rock, sedimentary rock and metamorphic rock) may be broken down into small particles to create soil. There are three types of weathering mechanisms: physical weathering, chemical weathering, and biological weathering. Some human activities such as blasting, waste disposal etc. may also create soil. Sometimes deeply buried soils may be altered by pressure and temperature to become metamorphic or sedimentary rock, and if melted and solidified again, they become igneous rock.

Table 5.5: Types of weathering

Type of weathering	*Soil formation processes*	*Remarks*
Physical effects	Physical weathering (refer Fig. 5.2) means mechanical disintegration, includes temperature variation effects, rain water impact, water seepage in cracks, frost action and other similar mechanisms which influence soil formation methods.	Creating fractures in the rock due to temperature variation and mechanical effects and consequent reduction of rock size.
Chemical reactions	Chemical weathering includes carbonation, oxidation, hydration and dissolution of matter composing rock and soil. Clay minerals, for example, can be formed by weathering of feldspar. The most common mineral constituent of silt and sand is silica. Though feldspar is most common rock forming mineral, silicon is more prevalent in soils due to its stable crystalline structure and less solubility as compared to feldspar. The broken pieces of rock are called gravel (size 4.75 mm to 100 mm) and larger pieces known as cobbles and boulders.	Alteration of rock composition by various natural chemical processes in action.
Biological interactions	Vegetation adds organic matter to the mineral components thus forming a litter. So the amount of organic matter in the soil depends not only on the abundance of litters but also on the resistance of plant debris to bio-degradation. Indeed, microorganism through their own biological activity, transform the litters into CO_2, NH_4^+ and NO_3^- (mineralization). The organic residues become humic components (humification). Humification is a slow and complex process in which both soil microorganisms and non-biological physico-chemical reactions take part. The amount of organic matter in the soil is influenced by the difference in velocity between mineralization and humification processes.	Abundance of organic matter produces litter and biodegradation of plant debris is the main physico-chemical reactions. 

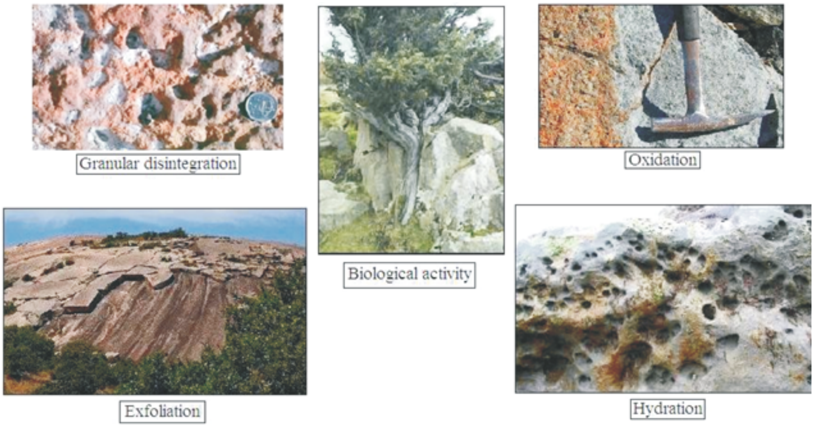


Fig. 5.2: Various types of weathering.

Table 5.6: Types of soil

Type of soil	*Characteristics of soil*
Ferruginous tropical soil	These soils are found in the northern part of the humid tropical zone which is characterised by the lateritic zone. They have been described by Aurbert (1951) in the zone of the Sudanese savana, by Maignien (1959) in northern Guinea and in Senegal and by Sieffwrmann (1959) in north Cameroon. The humid tropical zone is characterised by rainfall close to one metre per year and the humid season spread over five and six months. Unweathered minerals of the parent rock, especially potash or sodic feldspars are the constituent element of these soils. The clay fraction often shows kaolinitic types of clay minerals associated with iron hydroxide without free alumina. In alluvial zones soils show red to beige range of colours due to fractionation of minerals.
Mediterranean red soils	Red soils are found in many mediterranean countries. The greater part of these formations correspond to climatic conditions that no longer exist, as can be proved in many places by the development at their expense of a brown or leached soil at present. Rubefaction occurs today only in those special sites where rainfall is more abundant and microclimate contrast. It has been observed in Morocco, Oran and Portugal.
Calcimorphic soils	Calcimorphic soils which are not connected with limestone outcrops have in common an abundance in Ca and Mg ions saturating the absorptive complex of soils devoid of carbonates. The most famous examples are the black earths, of temperate steppes, such as those in the Ukraine and the Dakotas, calcimorphic soils of semi arid Mediteranean and sub-tropical

(*Contd.*)

Table 5.6: (*Contd.*)

Type of soil	*Characteristics of soil*
	American steppes, the tires of Morocco and of dark clays of the tropics, which are also called regurs or margallitic soils.
Lateiritic soils	Laterite is a weathered product of intertropical zone. It has been used with extremely varied meanings, but at present, this term is so widely used that it no longer has any pedologic significance, for the last hundred and fifty years.
Podazolic soils	This soil is characterized by soils evolved with raw materials and with rapid decomposition. Variation in mineralogical composition of clay fraction throughout the profile increases, chlorite decreases from bottom to top and subsequently intensity increases. Sometimes chlorite-vermiculite and illite-vermiculite mixed layers are present.
Calcareous brown soils	The argillaceous fraction of calcimorphic soils developed on limy parent rock shows little evolution in pedological profiles, many of which present a mineralogical composition which does not vary from the bottom to the top of profile.

5.6 SOIL MECHANICS

Soil mechanics indicates the behaviour of soil. Soil consists of a heterogeneous mixture of fluid and some solid particles. Fluid means usually air and water and on other hand solid means usually clay, silt, sand and gravel. Besides these some organic solids, liquids and gases also may be present, so soil is a heterogeneous mixture. Soil mechanism depends on genesis and composition of soil. Soil mechanics is used to analyze the deformations of flow of fluids within natural and manmade structures that are buried in soils. Example applications are building and bridge foundations, dams etc. Change of volume of soil due to squeezing water out of tiny pore spaces, also known as *consolidation*, *shear strength* and stiffness of soils. The shear strength of soil is primarily derived from friction between the particles and interlocking. Examples of geotechnical engineering applications of the principles of soil mechanics are slope stability, lateral earth pressure on retaining walls etc.

Functional relationship between normal stress and shear stress on a failure plane can be expressed in the following form

$$T_f = f(\sigma)$$

The linear function of normal stress is

$$T_f = c + \sigma \tan$$

where T_f is shear strength, c – cohesion, σ – normal stress on the failure plane and ϕ is angle of internal friction. This equation is called the Mohr-Coulomb failure criterion.

In saturated soil, the total normal stress at a point is the sum of the effective stress (σ') and pore water pressure (u)

$$\sigma = \sigma' + u$$

The Mohr-Coulomb failure criterion is expressed in terms of effective stress.

$$T_f = c' + \sigma' \tan \phi'$$

where c is cohesion and σ' is frictional angle, based on effective stress.

5.7 ATTERBERG LIMITS

The Atterberg limits are a basic measure of the nature of a fine-grained soil. Depending on the water content of the soil, it may appear in four states: solid, semi-solid, plastic and liquid. In each state the consistency and behaviour of a soil is different and so are its engineering properties. Thus, the boundary between each state can be defined based on a change in the soil's behaviour. The Atterberg limits can be used to distinguish between silt and clay, and it can distinguish between different types of silts and clays. These limits were created by Albert Atterberg, a Swedish chemist. They were later refined by Arthu Casagrande.

Some laboratory tests are listed below.

The values of these limits are used in various aspects. There is a close relationship between the limits and properties of a soil such as compressibility, permeability and strength. Thus the Atterberg limits are not only used to identify the soil's classification, but it also allows for the use of empirical correlations for some other engineering properties. Liquid limit test is to classify soils and to find the plasticity index of soil because different soils have various plastic limits. The shrinkage limit is much less commonly used than the liquid and plastic limits.

Table 5.7: Description of limits

Properties	*Description*	*Laboratory tests*
Shrinkage limit	The shrinkage limit is the water content where further loss of moisture will not result in any more volume reduction.	ASTM International D4943.
Plastic limit	The plastic limit is the water content where soil is in transition between brittle and plastic behaviour.	ASTM standard test method D4318
Liquid limit	The liquid limit is the water content at which a soil changes from plastic to liquid behaviour.	Fall cone test and Casagrande test

5.8 PLASTICITY INDEX

The plasticity index is a measure of the plasticity of a soil. The plasticity index is the size of the range of water contents where the soil exhibits plastic properties. The PI is the difference between the liquid limit and the plastic limit (PI = LL – PL). Soils with a high PI tend to be clay, those with a lower PI tend to be silt.

Table 5.8: Types of plasticity

PI	*0*	*(1-5)*	*(5-10)*	*(10-20)*	*(20-40)*	*>40*
Plasticity	Non-plastic	Slightly plastic	Low plasticity	Medium plasticity	High plasticity	Very high plasticity

5.9 ACTIVITY

It has been observed that the mineralogy of clay has direct relation with its geotechnical parameters. It is expected that clay mineralogy has got some direct bearing on the slope stability of a particular area containing those clays in the soil profile. As such, determination of the geotechnical parameters of clay, along with detailed clay mineralogy of the soils of the areas where slope stability problem have recorded, may be of importance for suggesting remedial measures or to eliminate the concerned area for construction of any important civil engineering structures. Some geotechnical properties to be studied:

- Detailed grain size analysis
- Consistency limits determination (L.L., P.L., P.I.)
- Swelling index
- Determination of dry density and optimum moisture content by proctor compaction (if adequate samples are available)
- Shear parameters, if sufficient sample is available.

On the basis of experimental evidence for several natural clay soils, the relationship between plasticity index and percent finer than 0.002 mm for any given clay was represented by a straight line passing through the origin and thus the activity of clay is defined by

$$A = \frac{\text{Plasticity index}}{\text{Clay content (percent finer than 0.002 mm)}}$$

where A is activity of clay.

On the basis of change of clay content, a modified definition of the activity of clay was proposed as follows:

$$A = \frac{\text{Change in plasticity index}}{\text{Corresponding change in clay content}}$$

The relationship between plasticity index and clay content is shown in Fig. 5.3. It shows that the slope of the line is different, from 10-40% , is a bit steeper compared to the other part (40-100%). At low clay content condition, presence of other non-clay minerals deviate the plasticity index trend from that of high clay content samples.

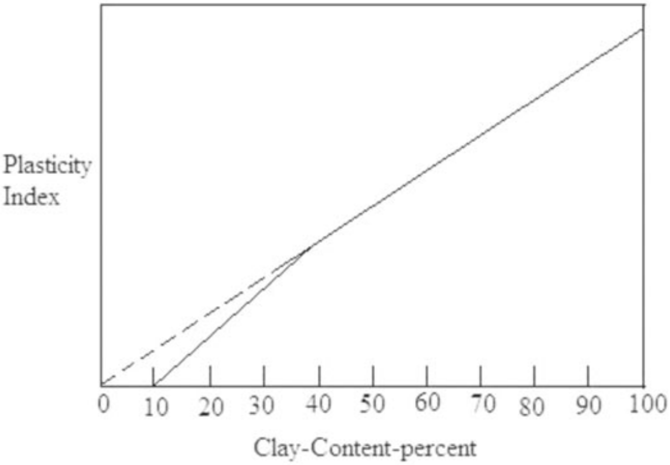


Fig. 5.3: Simplified relationship between plasticity index and clay content.

The direct linear relationship between PI and clay fraction content for any particular clay enables this degree of colloidal activity to be expressed very simply by the ratio:

$$\text{Activity} = \frac{\text{Plasticity index}}{\text{Clay fraction}}$$

This ratio is in fact the slope of the line.

Table 5.9: Types of clay with activity value

Type of clay	Activity
Inactive clay	<0.75
Normal clay	0.75-1.25
Active clay	>1.25

The relation between liquid limit and clay fraction, although linear, is not one of the direct proportion and is therefore less convenient than the ratio PI by clay fraction.

The three minerals – quartz, calcite and mica – tested by Von Moons, were ground to a very small particle size and the PI then determined on the fraction finer than two microns. The activity of these minerals is low, as might be expected from their relatively simple crystal structure. Illite is probably the most widespread of all clay minerals but it usually occurs in conjunction with other minerals. The clay known as bentonite consists almost exclusively of the mineral montmorillonite. In its natural state bentonite is usually a sodium clay

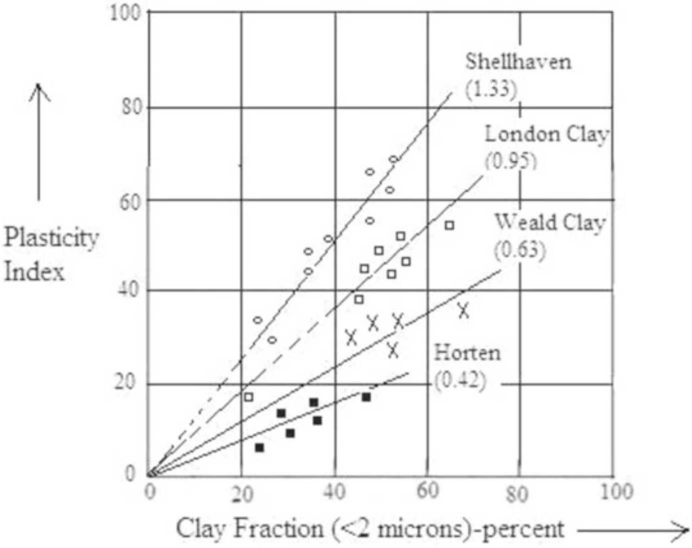


Fig. 5.4: Relation between plasticity index and clay fraction.

Table 5.10: Activity of various minerals

Mineral	*Activity*	*Reference*
Quartz	0.0	Von Moos (1938)
Calcite	0.18	Von Moos (1938)
Mica (muscovite)	0.23	Von Moos (1938)
Kaolinite	0.46	Samuels (1950)
Illite	0.90	Northey (1950)
Ca-montmorillonite	1.5	Samuels (1950)
Na-montmorillonite	7.2	Samuels (1950)

and, in this state, it has a very exceptionally high activity. By effecting a base exchange from sodium to calcium, Samuels (1950) has shown by repeated tests that the activity is considerably lowered; although even the Ca-bentonite has high activity. He has also shown that bentonite carrying a tri-valent base Al has an activity of about 1.3. No base exchange tests appear to have been made on illite, since this material shows moderate activity. It is clear from the above results that activity is, broadly speaking, related to the structural complexity of the minerals: ranging from quartz through kaolin up to montmorillonite.

Concluding Remarks

Industrial application of most of the clays directly depends on their physical properties. This chapter prepared a background for the studies of industrial application of clays in Part II. Beside this the chapter highlights the relation between weathering and soil formation.

QUESTIONS

1. Different types of weathering depend on particular agents; explain it.
2. Soil generation is closely related with weathering; give examples of various types of soils.

FURTHER READING

Andrew, N. and Thomas Telford (2006). Disturbed soil properties and geotechnical design. Schofield. ISBN 0-7277-2982-9.

Buol, S.W., Hole, F.D. and McCracken, R.J. (1973). Soil Genesis and Classification (1st ed.), Iowa State University Press, Ames, IA.

Chesworth (Edited by Ward) (2008). Encyclopedia of soil science. Springer, Dordrecht, Netherland.

Dixon, D.W. (1983). Radiation hazards to collectors of geological specimens containing natural radioactivity. National Radiological Protection Board Report 131 (UK).

Dooley, Alan (2006). Sandboils 101: Corps has experience dealing with common flood danger. Engineer Update. US Army Corps of Engineers.

Ehlers, Ernest G. and Blatt, Harvey (1982). Petrology: Igneous, Sedimentary and Metamorphic. W.H. Freeman and Company, San Francisco.

Guggenheim, Stephen and Martin, R.T. (1995). Definition of clay and clay mineral. Joint report of the AIPEA nomenclature and CMS nomenclature committees. *Clays and Clay Minerals*, **44(5):** 713-715.

Holtz, R.D. and Kovacs, W.D. (1981). An Introduction to Geotechnical Engineering. Prentice-Hall, Inc.

Jones, J.A.A. (1976). Soil piping and stream channel initiation. *Water Resources Research*, **7(3):** 602-610. Bibcode 1971WRR... 7...602J. doi:10.1029/WR007i003p00602.

Klein, C. and Hurlbut, C.S. (1993). Jr. Manual of Mineralogy (21st ed.). John Wiley and Sons, New York.

Kunze, G.W. (1952). Weathering of micas and their role in potash fixation. Ph.D. Thesis. Pennsylvania State College.

Mitchell, J.K. and Soga, K. (2005). Fundamentals of soil behavior (3rd ed.). John Wiley and Sons, Inc. ISBN 978-0-471-46302-7.

Nassau, K. (1978). The origin of color in minerals. *American Mineralogist*, **63:** 219-229.

Parkins, Dextral (2002). Mineralogy (2nd ed.). Prentice-Hall of India, New Delhi.

Poulos, S.J. (1989). Advance Dam Engineering for Design, Construction and Rehabilitation: Liquefaction Related Phenomena. Jansen, R.B. (ed.). Van Nostrand Reinhold.

Ronald James Northey (1950). Plasticity Index.

Santamarina, J.C., Klein, K.A. and Fam, M.A. (2001). Soils and Waves: Particulate Materials Behavior, Characterization and Process Monitoring. Wiley. ISBN 978-0-471-49058-6.

Taylor, S.A. and Ashcroft, G.L. (1972). Physical Edaphology.

Terzaghi, K. (1943). Theoretical Soil Mechanics. John Wiley and Sons, New York.

Terzaghi, K., Peck, R.B. and Mesri, G. (1996). Soil Mechanics in Engineering Practice (3rd ed.). John Wiley & Sons, Inc.

Waltham, T. (2001). Foundations of Engineering Geology (2nd ed.). Taylor & Francis.

William, Lambe T. and Whitman, Robert V. (1991). Soil Mechanics. ISBN 978-0-471-51192-2.

Wood, David Muir (1990). Soil Behavior and Critical State Soil Mechanics. Cambridge University Press. ISBN 0-521-33249-4.

Yang, X.S. (2008). Mathematical Modelling for Earth Sciences. Dunedin Academic Press.

Zussman, J. (1977). Physical Methods in Determinative Mineralogy. Academic Press, New York.

CHAPTER

6

ANALYTICAL TECHNIQUES FOR CLAY STUDIES

Analytical techniques extract various information like the internal structure, elemental composition, valency state of specific ions, thermal interaction etc. of clay minerals. For multipurpose application these data can be used suitably.

6.1 DIFFERENT ANALYSES AND THEIR USES

To identify a material under study, its various properties are analyzed using different techniques. Analytical techniques utilize the interaction of incident entity (in the form of electromagnetic waves of different frequencies or particles like electrons etc.) with the sample to get the relevant information through detailed analysis of the output data.

For spectroscopic analysis (e.g. XRF, XRD, IR, Raman, Mossbauer etc.), a plot of the observed intensity versus the corresponding wavelength or frequency (or some other related parameter) is called the spectrum of that particular analytical method. The spectrum or the data obtained from such experiments contain information about nature of the interactions, atomic and molecular energy levels, chemical bonds, crystallographic information and other related processes. When only the item of interest is identified, it is called qualitative analysis and when the amount present is estimated, it is known as quantitative analysis. The effect of heat on a sample is reflected through its variation of thermodynamic properties. Such studies are done by thermal analysis.

The analytical techniques used for various types of clay studies have a long list. Due to the fine grain and opaque nature of clays, usual optical microscopic techniques are not applicable. But the high resolution electron microscopy (e.g. scanning and transmission type) is a very useful tool to

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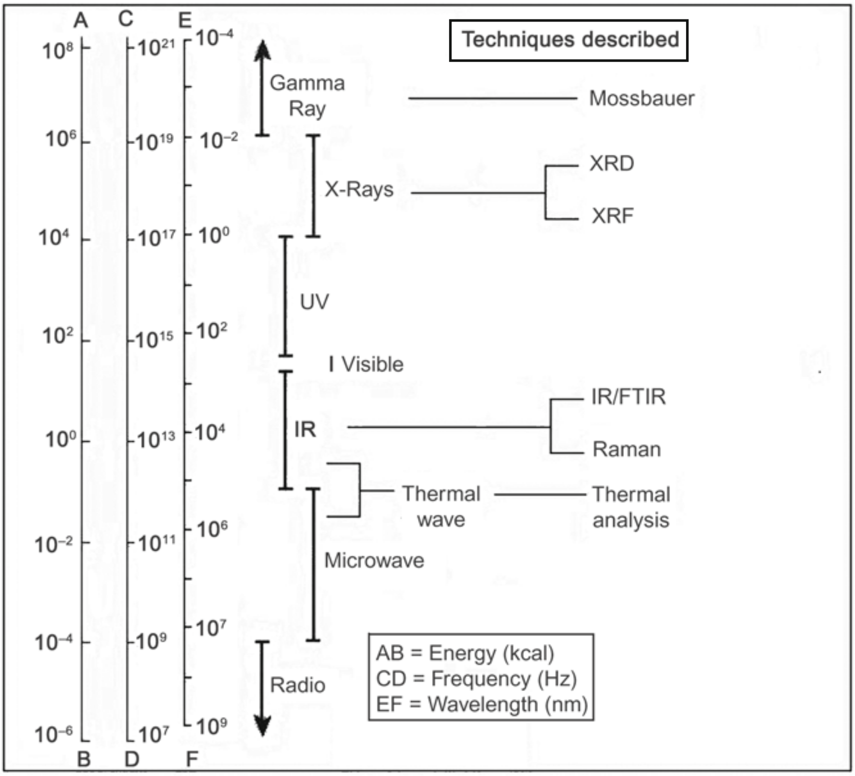

Fig. 6.1: Electromagnetic radiation and related analytical techniques.

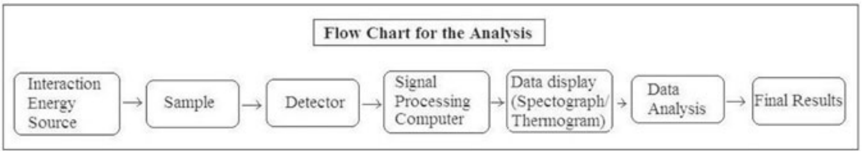

Fig. 6.2: A flow chart depicting the different analytical processes.

understand some pertinent features of clays. Clays can be uniquely identified by the finger print of their crystalline structures with X-ray powder diffraction technique. For elemental analysis (i.e. chemical composition), X-ray fluorescent is a very powerful tool. Study of infrared (IR) and Raman spectra yields information about the chemical functional groups and types of bonds present in the sample. For information regarding the valence state of iron Mossbauer spectroscopic analysis is unique and very useful for clay studies.

The accuracy and precision of data from any technique is of vital importance. The experimental results would be accurate if they show their proximity to the true values while the precision is connected with the reproducibility of the results under repeated measurements.

Table 6.1: Analytical techniques with their specialties

Name of the technique	*Principle of operation*		
X-ray analysis	XRD	Analyses and identifies crystalline samples clay, using standard file.	
		Analyses and identifies elements from its fluorescent characteristic x-rays.	
		EXD (Energy dispersive x-ray)	Output data recorded as energy of the emitted x-ray vs. corresponding line intensities.
		WDX (Wavelength dispersive x-ray)	Output data presented as the emitted x-ray wavelength vs. its intensities.
Electron microscopy	Electron beams replaces the visible light to increase its magnification and resolution. Focussing is done using magnetic lenses.		
	TEM	Electron beam passes through the sample and the interactions are recorded for further analysis.	
	SEM	Electron beam scans the surface of the sample and interactions are recorded for further study.	
Electron probe microanalyser (EPMA)	Electron beam is allowed to probe the sample resulting interactions, emits characteristics x-ray of elements present in the sample recorded in WDX-spectra and the needed information can be extracted from the data.		
Infrared analysis	Used to identify the chemical functional groups present in the sample and also the types of bonds in it by detecting the absorption spectra of vibrational levels of atoms or molecules.	FTIR	In a dispersive IR-Spectrometer, component frequencies are viewed individually with Fourier Transform IR. All frequencies are simultaneously examined in much more details.
Raman spectroscopy	In the technique, sample is exposed to a lesser beam and the scattered light is collected from the data i.e., wavelengths and intensities of the scattered light. The information about the functional groups in a molecule can be identified.		

(*Contd*)

Table 6.1: (*Contd*)

Thermal analysis	It is the change of different properties of a material with the variation of temperature.		
	Thermo gravimetry (TG)	Mass change study.	Simultaneous thermal analysis (STA) [(TG)+(DSC)]
	Differential Scanning Calorimetry (DSC)	Study of heat difference	
	Dilatometry (DIL)	Volume change analysis	
	Evolved gas analysis (EGA)	Study of gaseous products on decomposition	
	Laser flash analysis (LFA)	Thermal conductivity and thermal diffusivity study	
	Thermo mechanical analysis (TMA)	Variation of dimension analysis	

6.2 X-RAY TECHNIQUES

In X-ray analytical techniques, a suitable metal target is exposed to a beam of electrons which excites the atoms of the target. De-excitation of the atom may occur in three ways, illustrated in Figs 6.3 and 6.4.

It is to be noted that the peak of the curve shifts towards low wavelength side with increase of incident electron energy.

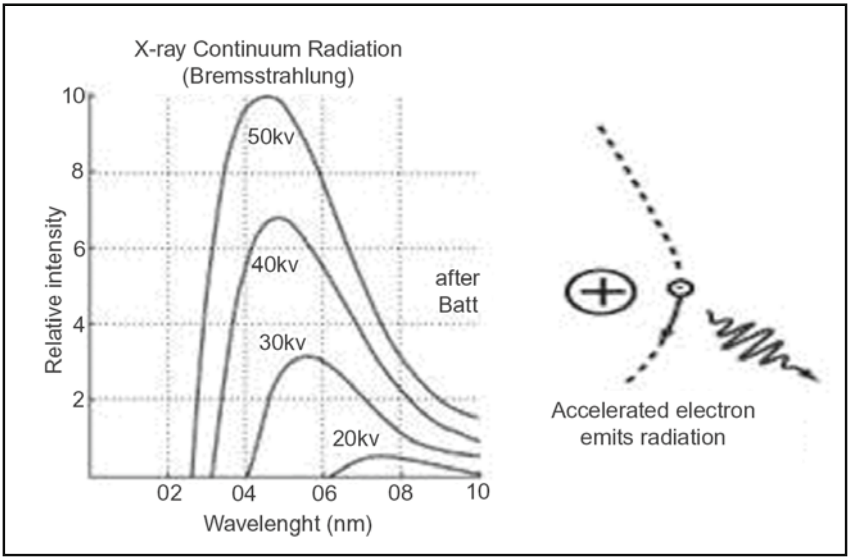

Fig. 6.3: Energy dependence of X-ray production.

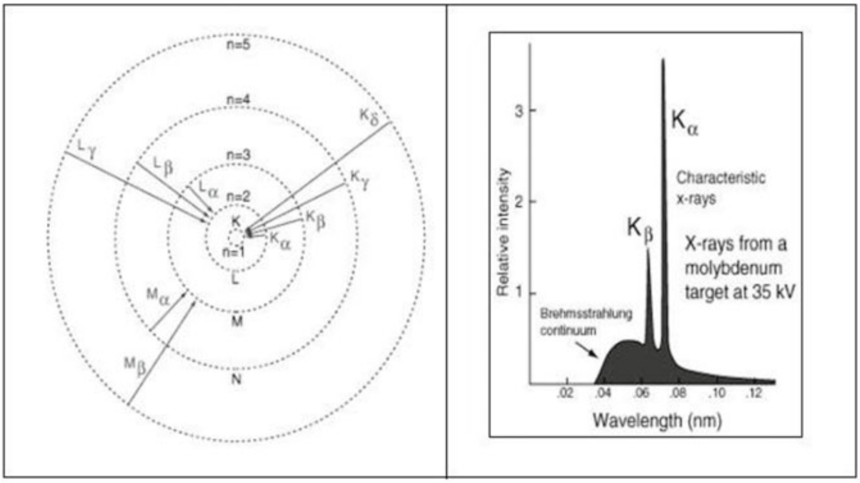

Fig. 6.4: Atomic orbital and characteristic X-ray emission.

Emission of X-rays

X-rays are generated by large energy transition of electrons within an atom from outer orbital to core orbitals. The x-ray emissions associated with these transitions are called characteristic x-rays. The labels on the illustration show the historical labelling of characteristic x-ray transitions.

Characteristic X-rays

The x-ray emissions associated with these transitions are called characteristic x-rays. The labels on the illustration show the historical labeling of characteristic x-ray transitions.

"Auger" Electron

The excitation energy from the inner atom is transferred to one of the outer electrons causing it to be ejected from the atom.

Sometimes, as the atom returns to its stable condition, instead of emitting a characteristic x-ray it transfers the excitation energy directly to one of the outer electrons, causing it to be ejected from the atom. The ejected electron is called an "Auger" electron. This process is a competing process to XRF. Auger electrons are more probable in the low Z elements than in the high Z elements.

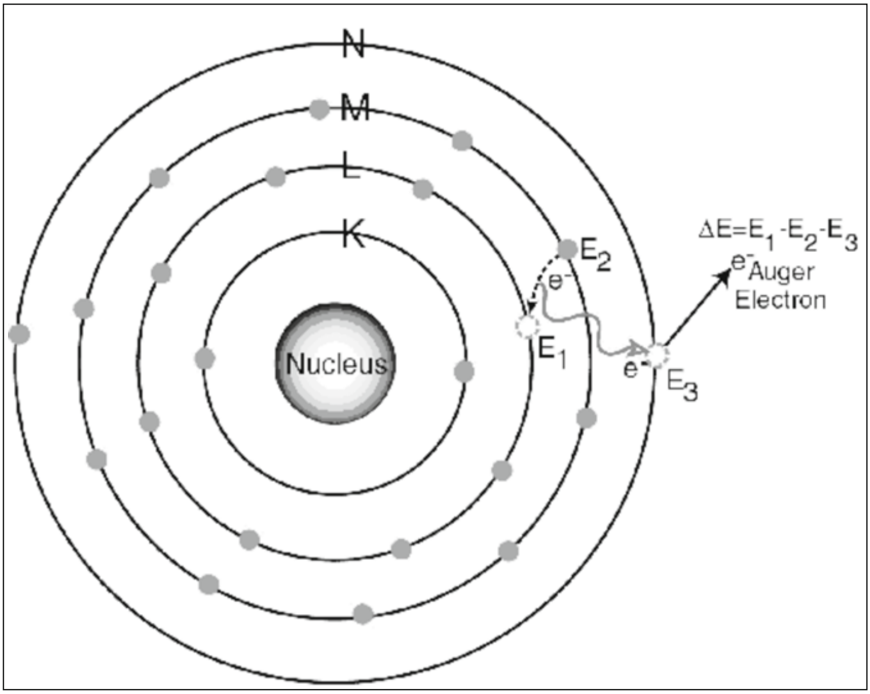

Fig. 6.5: Diagram of Auger electron.

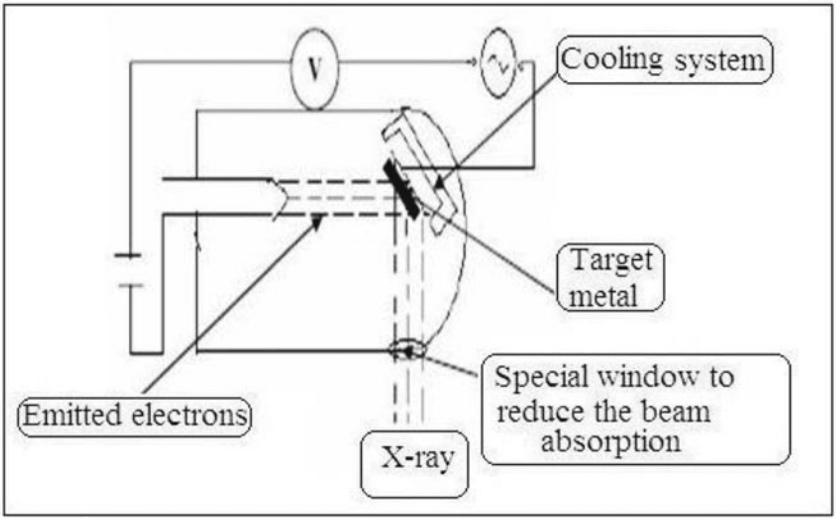

Fig. 6.6: Production of x-rays in the lab.

Table 6.2: Characteristic wavelength for common analytical x-ray tube target

Target metal	*Kα (Angstrom)*	*Kβ (Angstrom)*
Iron	1.94	1.76
Copper	1.54	1.39
Molybdenum	0.709	0.632
Chromium	2.29	2.08
Nickel	1.66	1.50
Cobalt	1.79	1.62
Silver	0.559	0.497

Properties of X-rays

1. The x-rays, like light, are *electromagnetic radiations* of extremely short wavelength (100-0.0001A).
2. Obeys laws of reflection, refraction, interference, diffraction and also polarisation under suitable conditions.
3. They travel in straight lines like light, *unaffected by electric and magnetic fields*, indicating they are not charged particle beams, like cathode rays.
4. X-rays affect (blacken) photographic plate and the degree of blackening depends on the intensity of radiation. For this property, photography is a very suitable technique to detect/study x-rays.
5. The x-rays are having high penetrating power. The shorter the wavelength, greater the penetration power. For low density substances, the penetration is more compared to the high density ones. Usually passes through matter that are opaque to visible rays.

6. Soft (long wave length) x-rays are absorbed by materials to varying degrees; this property is used in the radiography of substances.
7. The living cells can be destroyed by x-rays of suitable intensity.
8. X-rays ionise gases through which it pass and the ionising power depends on the intensity of the radiation. This property is used to measure the intensity of x-rays—used for x-ray detection and measuring intensity.
9. X-rays cause fluorescence in many substances (e.g. ZnS, Ca-salts etc.) and are used as a distinct property for identifying such materials.
10. X-rays exibit corpuscular nature. Compton effect is the confirmation of this property.
11. Various analytical techniques have been developed utilising the above mentioned properties e.g. x-ray absorption, emission spectroscopy, x-ray diffractrometry etc.

Process of X-ray Analysis

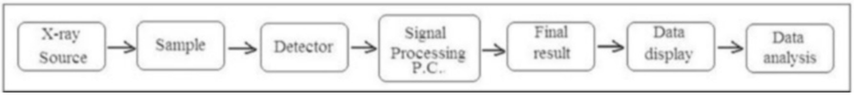

Fig. 6.7: Flow chart for the x-ray analysis.

6.3 X-RAY POWDER DIFFRACTION (XRD)

This is a non-destructive method to analyze crystalline phases of the samples. Comparing with standard data file the phases present in a sample can be exactly identified. Now a days, analytical softwares and needed data files are available with the Diffractometer Unit.

The technique can be understood following the sequence. (1) Basics of x-ray crystallography; (2) Bragg's Law; (3) Geometry of diffraction; (4) Sample preparation techniques; (4) General uses e.g. identification of unknown phases, their qualitative and quantitative estimation, grain-size analysis, crystallinity study, effect of temperature and pressure variation on crystalline phases etc. and (5) Basic errors for x-ray diffraction data.

Basics of X-ray Crystallography

Knowledge of basic crystallography starts from the conception of symmetry, symmetry planes and symmetry operations necessary to identify the parameters, like lattice, lattice planes, crystal lattices (i.e. Bravis lattice) describing different crystal symmetries. Miller indices (*h*, *k*, *l*) to identify crystal planes etc. are explained here.

Table 6.3: Different symmetry operation used in crystallography

Symmetry operation	*Symmetry element*	*Symbols*
Rotation around an imaginary axis passing through centre	*Rotation axis or symmetry axis*	**1, 2, 3, 4, 6**
Reflection across a plane	Plane of symmetry or mirror	*m*
Inversion through a centre	Inversion point or centre of symmetry	*i* or *c*
Combined operation of rotation around an axis followed by inversion through the centre.	Roto-inversion axis	A1, A2, A3, A4, A6

Crystal Systems etc.

A crystal has an array of points with repetitive arrangement in three dimensions. These points may be atoms, ions or molecules and the arrangement is called the Lattice. A combination of lattice and crystal system makes fourteen possible Bravais Lattices. A unit cell is the smallest volume which keeps all the properties of the crystal, e.g. chemical, physical and geometrical. A unit cell must contain enough of the various atoms to establish the chemical formula, the pattern of arrangements and the directional properties of the crystal structure.

Seven Types of Crystal Lattices (Bravais Lattices)

The crystal lattices parameters are the unit cell dimensions e.g. a, b, c. The angle between the axes are α, β and γ. The different types of crystals can be described in the framework of Bravis Lattices as shown in Fig. 6.8.

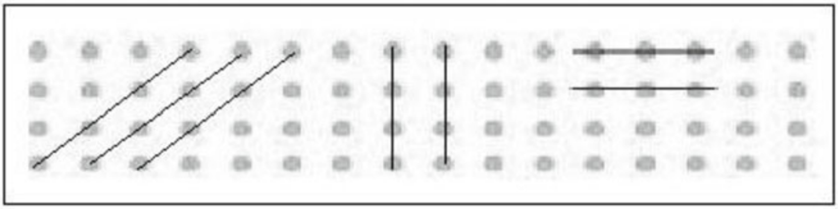

Fig. 6.8: Lattice and crystal planes in two dimensions.

Each cell must be of size and shape in relation to the atoms it contains. When many cells are stacked in three dimensions, every cell will be surrounded by exactly similar cells with no gaps whatsoever between them.

Miller Indices

The Miller indices describes the different planes in the crystal with respect to its axes, and denoted by *h* (for axis x or a), *k* (for axis y or b) and *l* (axis z or c). The corresponding planes are denoted by *d* (*h k l*). Thus, the lattice constants are a, b, c, α, β, γ and Miller indices are *h*, *k*, *l*.

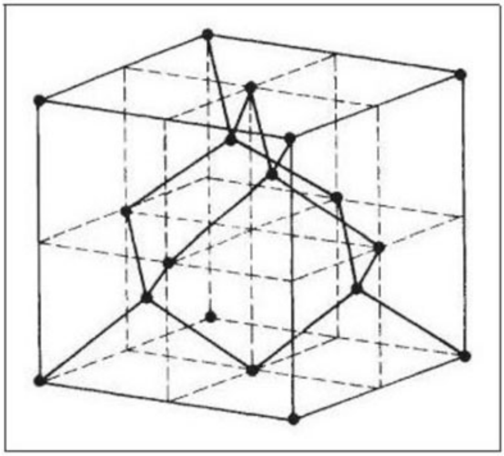

Fig. 6.9: Lattice and unit cell of diamond.

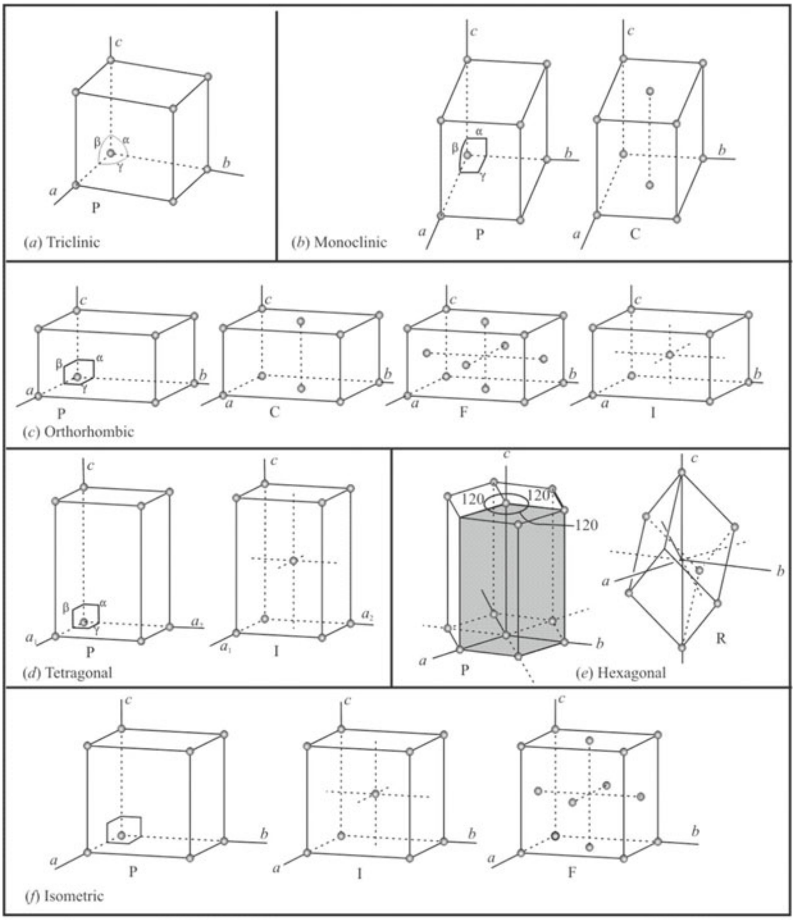

Fig. 6.10: Seven types of crystal lattices.

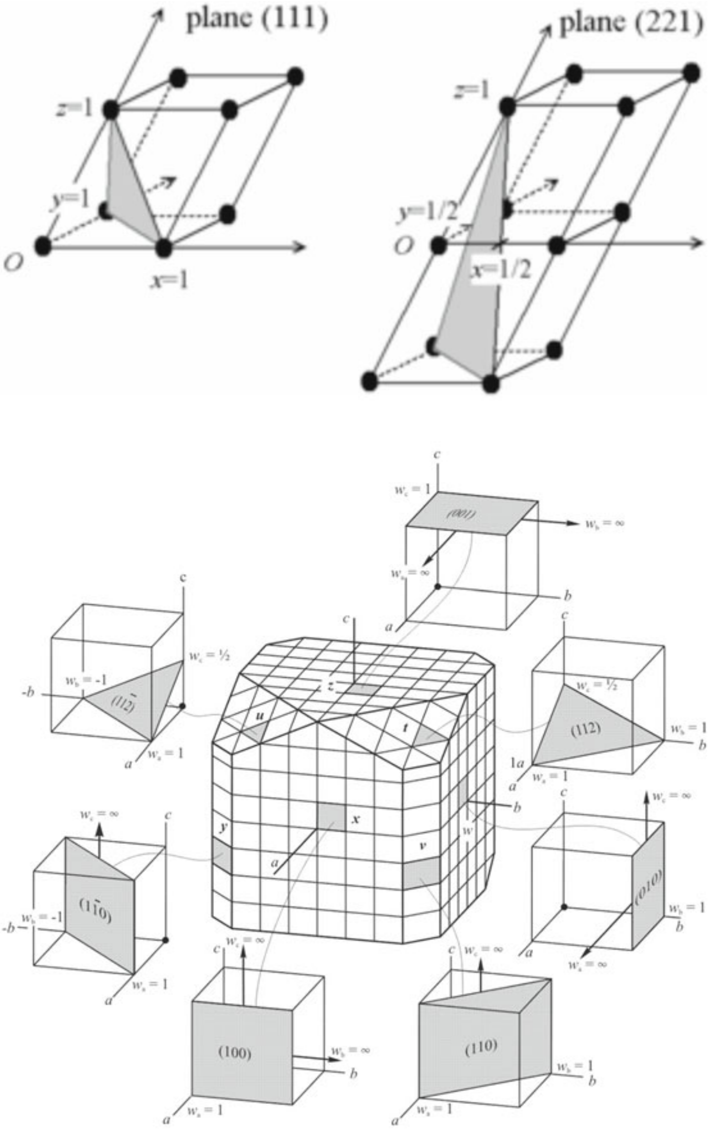

Fig. 6.11: The planes with their Miller indices.

Bragg's Law for Diffraction of X-rays from Crystal Planes

Diffraction phenomena occur when wave faces an obstacle of similar dimension to its wavelength. Since the atomic dimensions are of same order of magnitude of the X-ray wavelength, X-ray diffraction occurs with atomic crystals. This phenomenon is excellently formulated by Sir W.L. Bragg and known as Braggs‘s Law.

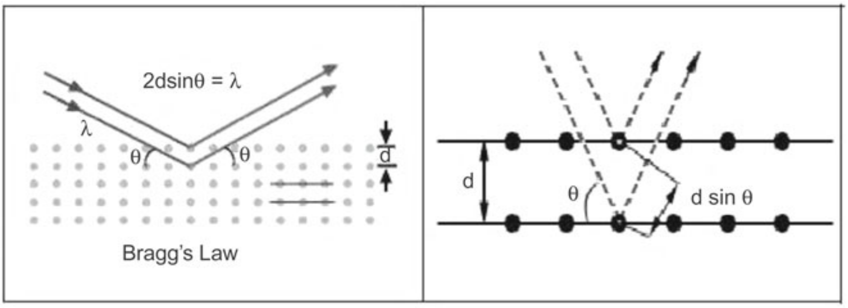

Fig. 6.12: Principles of Bragg's law.

Any crystal plane *d* is identified by the Miller Indices *h*, *k*, *l* and accordingly, Braggs law can be written as

$$2d_{h\,k\,l}\sin\theta_{h\,k\,l} = n\lambda$$

Geometry for X-ray Diffraction Data Collection

In the Bragg-Branton geometry of diffractometer, if the sample rotates by angle θ the diffracted beam rotate by angle 2θ. Goniometer circle correlate the positions of the sample, detector and the incident beam. By rotating the sample (kept in a holder), the scanning angle can be varied as desired and the rotation speed of the sample can also be adjusted. The sample chamber may have the temperature and pressure controlling system for suitable use.

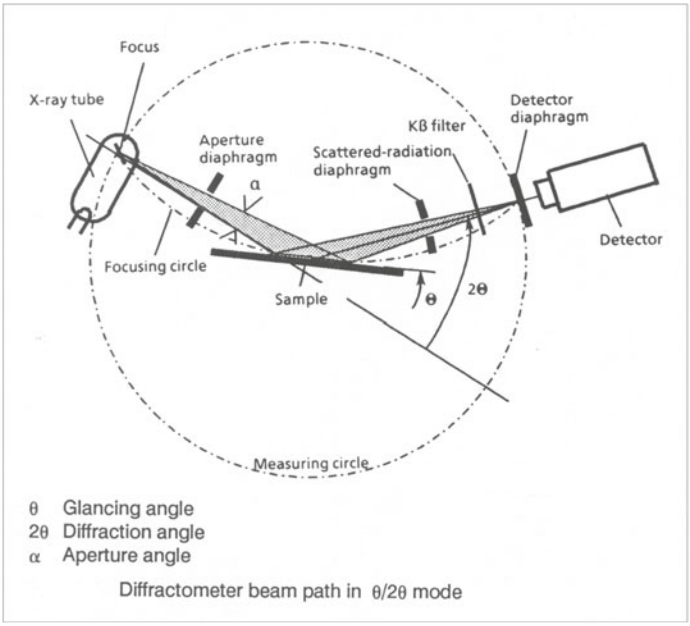

Fig. 6.13: Bragg-Brenton powder diffractometer: components and geometry.

Sample Preparation Techniques and Powder Diffraction Analysis for Identification

The sample is to be taken in powder form (about 200 meshes), the powder is to be packed in the sample holder and to be pressed slightly for right packing. No rubbing to be done while packing sample which creates preferred orientation of the grains.

Identification of any phase is done using standard data files with search match software program to identify various peaks in the diffractogram.

Applications of Powder Diffraction

1. Qualitative analysis
2. Quantitative analysis
3. Crystal structure determination
4. Crystallite size
5. Microstrain
6. Residual macrostresses
7. Thin films
8. Crystallinity

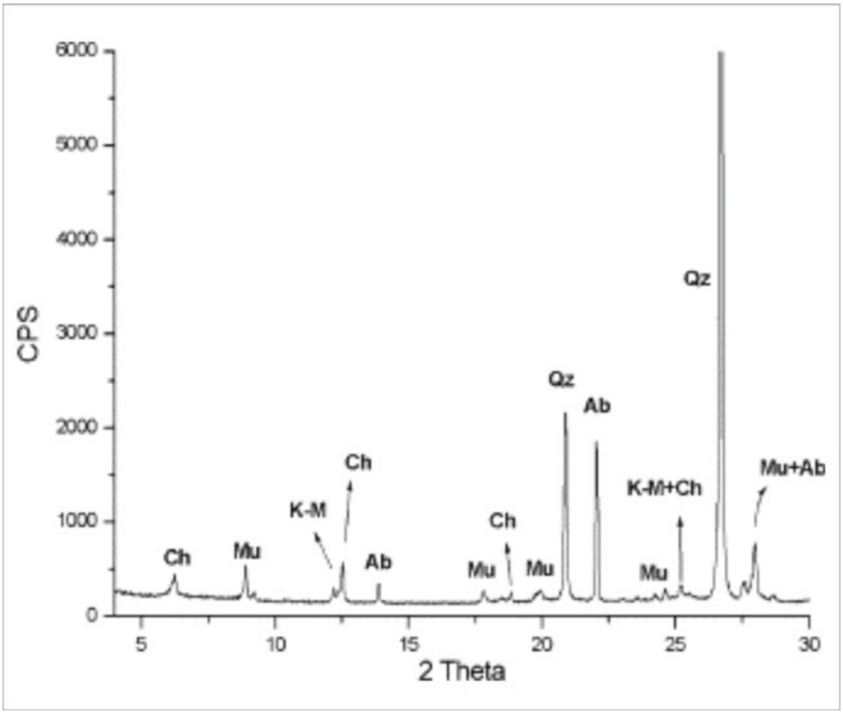

Fig. 6.14: X-ray powder diffraction pattern from the soil samples (fraction size 2 μm); the mineral phases are: chlorite (Ch), muscovite (Mu), kaolinite-montmorillonite (K-M), albite (Ab), quartz (Qz).

9. Studies of phase diagrams: (A) Phase boundaries, (B) Solid solutions and (c) Phase transitions
10. Studies of chemical reactions and identification of reaction products.
11. Determination of grain sizes
12. Preferred orientation in polycrystalline bodies.

6.4 X-RAY FLUORESCENCE (XRF)

High energy radiation (x-rays or soft gamma rays) falling on a solid target generate inner shell vacancies which are being filled up from outer shells producing secondary characteristic x rays. This is known as x-ray fluorescence (XRF). The phenomena is of intense use for element detection i.e. chemical analysis of solids like metals, ceramics, building materials and even glass. This technique is widely used in geochemical research, archaeology and in forensic science.

XRF spectroscopy is a non-destructive and fast technique used for both qualitative and quantitative elemental analysis. This method has a fairly uniform detection limit of elements heavier than fluorine with a wide range of concentration, e.g. 100% to parts per million.

The XRF method is widely used to measure the elemental composition of materials. Since this method is fast and non-destructive to the sample, it is the method of choice for field applications and industrial production for control of materials. Depending on the application, XRF can be produced by using not only x-rays but also other primary excitation sources like alpha particles, protons or high energy electron beams.

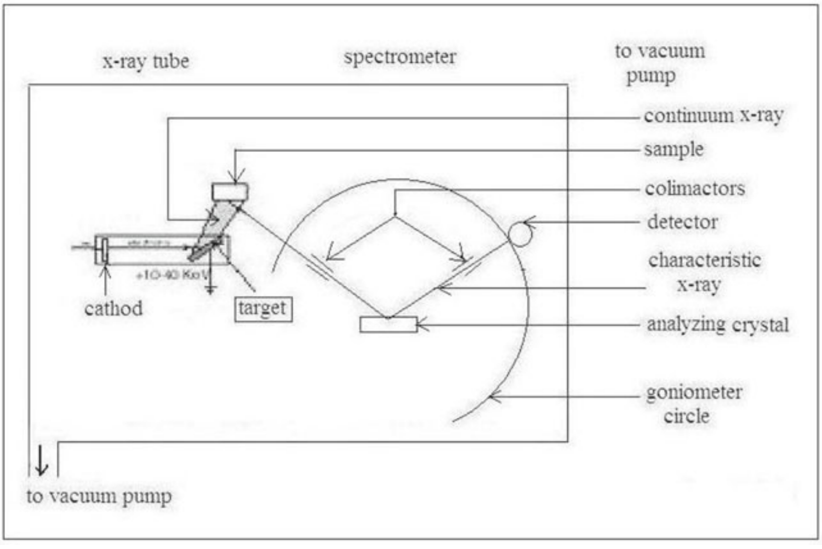

Fig. 6.15: The XRF spectrometer measures the individual component wavelengths of the fluorescent emission produced by a sample when irradiated with x-rays.

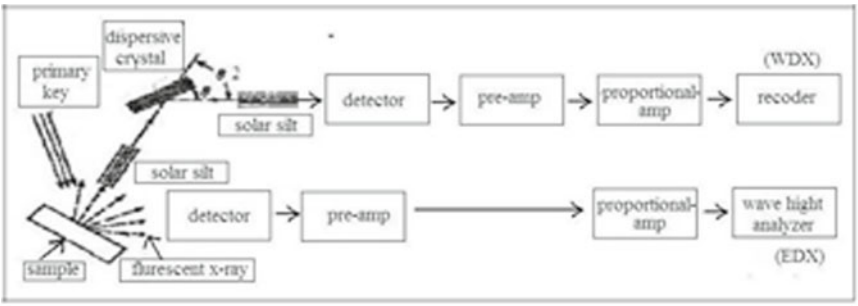

Fig. 6.16: Schematic diagram of energy dispersive and wavelength dispersive XRF spectrometers.

WDXRF

WDXRF (wavelength dispersive x-ray fluorescence) separation is achieved by diffraction, using an analyzer crystal that acts as a grid. The specific lattice of the crystal selects the correct wavelengths according to Bragg's law. A WDXRF spectrometer provides: the advantages of total application, versatility optimal measurement conditions programmable for each element, excellent light-element performance, very high sensitivity and low detection limits.

EDXRF

EDXRF (energy dispersive x-ray fluorescence) spectrometry works without a crystal. An EDXRF spectrometer includes special electronics and software modules to take care that all radiation is properly analyzed in the detector. It provides a lower cost alternative for applications where less precision is required. The high-end uses the 3D EDXRF techniques featuring a 3-dimensional, polarizing optical geometry.

XRF technique is suitable for bulk chemical analysis of major elements e.g. Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and P. For trace element analysis with abundances >1 ppm can also be done for Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Rb, Sc, Sr, Rh, U, V, Y, Zr and Zn with a detection limit of few ppm. For materials which are compositionally similar, suitable standards are available. Samples containing high abundances of elements corrections are to be made for absorption and fluorescence effects. XRE is commonly used to identify traces and for quantitative estimation, good resolution of the peaks are necessary. It can also analyze thin films.

As in case of x-ray fluorescence (XRF) techniques, in case of EDXRF also, other similar competing techniques are AAS (Atomic Absorption Spectroscopy), ICPS (Inductively Coupled Plasma Spectroscopy) and NAA (Neutron Activation Analysis). Modern XRF-analytical units, for its multi elemental run, is fast and cost effective.

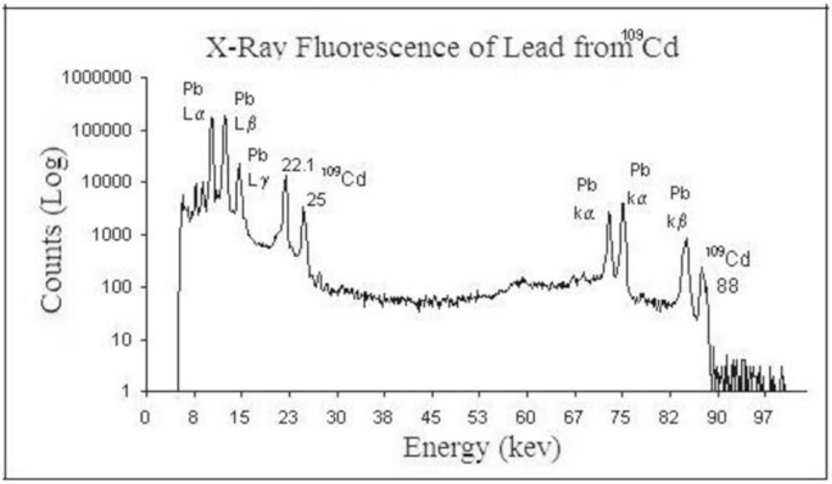

Fig. 6.17: A typical XRF spectra.

Applications of X-ray Fluorescence Technique

X-ray fluorescence technique, with its bulk and trace element detection capability, has a wide application field. More specifically, it is particularly well-suited for investigations in chemicals, coatings and thin films, mining (e.g., measuring the grade of ore), ceramic and glass manufacturing, metallurgy (e.g., quality control), environmental studies (e.g., analyses of particulate matter on air filters), Petroleum industry (e.g., sulphur content of crude oils and petroleum products), field analysis in geological and environmental studies (using portable, hand-held XRF spectrometers), cement production, forensics, pharmaceutical applications, in plastics, polymers and rubber industries, etc.

6.5 ELECTRON MICROSCOPY

The resolving power of a microscope is its ability to resolve the images of two points close to each other and expressed as $R = 1/d\theta = D/1.22\lambda$ where D is the aperture of the objective and λ is the wavelength of the light. By reducing wave length, i.e. increasing the frequency of the radiation, resolving power of the microscope can be increased. A high resolution microscope was designed replacing visible light by electron beam.

In electron microscopy (EM), a focussed beam of electrons are used (replacing visible light in optical microscope) to bombard the sample for getting information about its structure and composition. This improves the possible magnification to ~2,000,000.

Interaction with Matter

Electron bombardment in a material produces the effects as shown in Fig. 6.18.

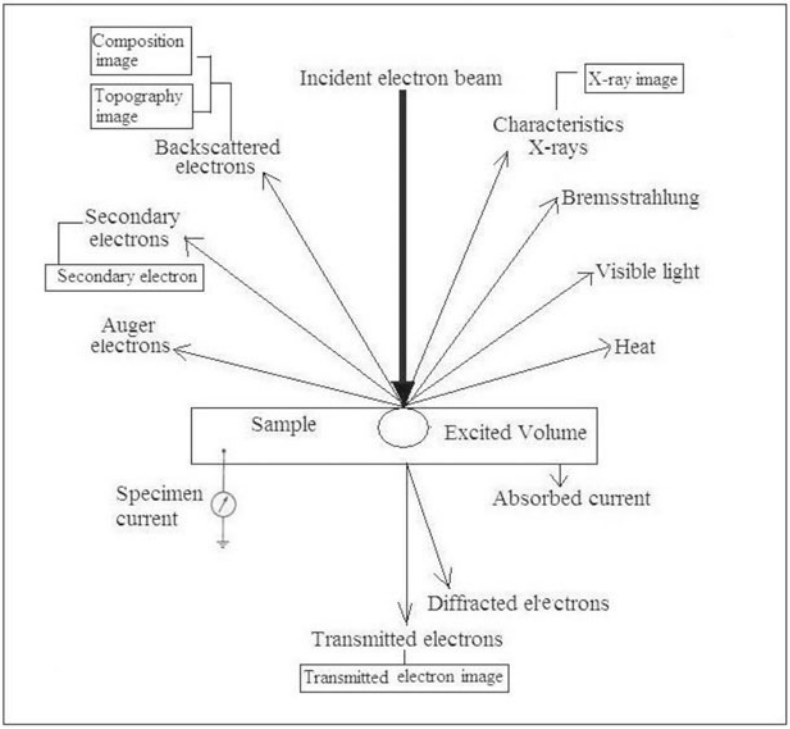

Fig. 6.18: Effects produced by electron bombardment to a material.

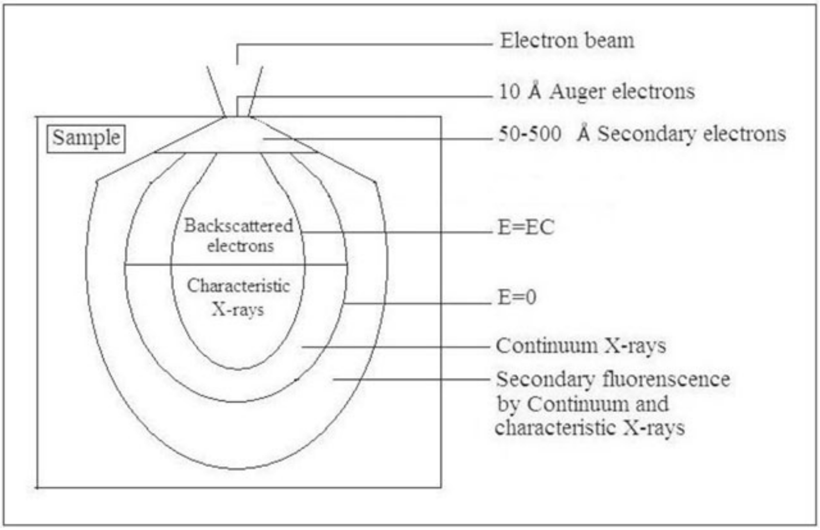

Fig. 6.19: Generalized illustration of interaction volumes for various electron-specimen interactions. Auger electrons (not shown) emerge from a very thin region of the sample surface (maximum depth about 50 Å) than do secondary electrons (50-500 Å).

The different types of electrons used for analysis:

(a) Topography and composition**:** Backscattered electrons
(b) Topography: Secondary electrons, Auger electrons
(c) Structure and composition: Transmitted electrons
(d) Composition: X-rays, photons

Working principle of Electron Microscope (EM)

(i) A source producing electrons and then accelerated (by using a positive potential) towards the sample.
(ii) The beam is focussed to a monochromatic one using apertures and magnetic lenses.
(iii) The magnetic lenses finally focus the beam on the sample.
(iv) The strong interact with the beam starts.
(v) Using EDX or WDX, the acquired data get analyzed.

The types of electron microscopy:

1. Scanning electron microscopy (SEM)
2. Transmission electron microscopy (TEM)
3. Reflection electron microscope (REM)
4. Scanning transmission microscope (STEM)
5. Low voltage electron microscope (LVEM)

Main Observations Made with these Microscopes

(a) Topographic analysis i.e. surface features, textures and the correlation between them, property of materials like reflectivity, hardness etc.
(b) Morphological studies i.e. relation between the structures e.g. shape, size etc., properties like ductility, strength, reactivity etc. of materials.
(c) Composition determination i.e. qualitative and quantitative analysis of elements and compounds present in the sample. These data help to understand the material properties like melting point, reactivity, hardness etc. with the composition.
(d) Crystallographic information i.e. relating the material properties like strength, conductivity, electrical properties etc. with the crystal structure of the compounds.

Scanning Electron Microscope

A focussed (using magnetic lenses) electron beam falls on the sample surface kept in vacuum. The beam then scans over the sample surface and the scattered electrons detected and collected to have the information about the sample surface.

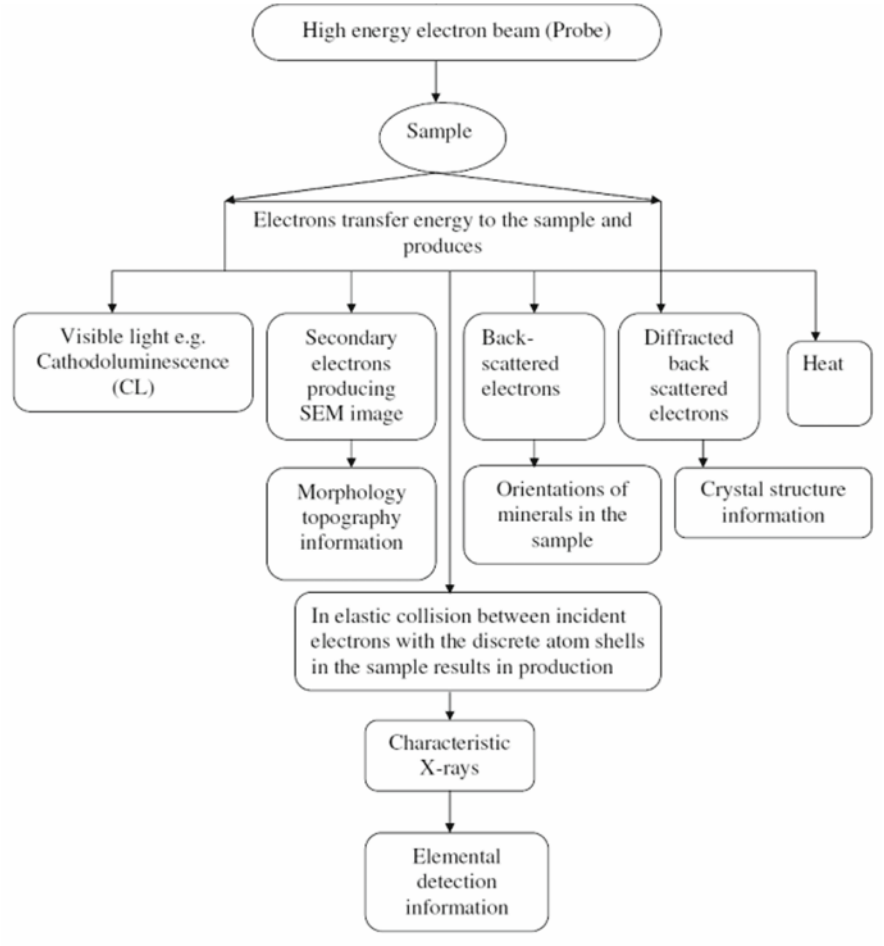

Fig. 6.20: Flowchart of function of SEM.

6.6 TRANSMISSION ELECTRON MICROSCOPY (TEM)

A high energy electron beam (~100 to 400 keV), collimated by magnetic lenses pass through a sample under high vacuum. The transmitted beam and part of the diffracted beam form a resultant diffraction pattern and an image is formed on the fluorescent screen kept below the specimen. This magnified images yields information about the size, shape etc. of the micro-structural constituents of the material under study. High-resolution image, that contains information about the atomic structure of the material, can be obtained by recombining the transmitted beam and diffracted beams together.

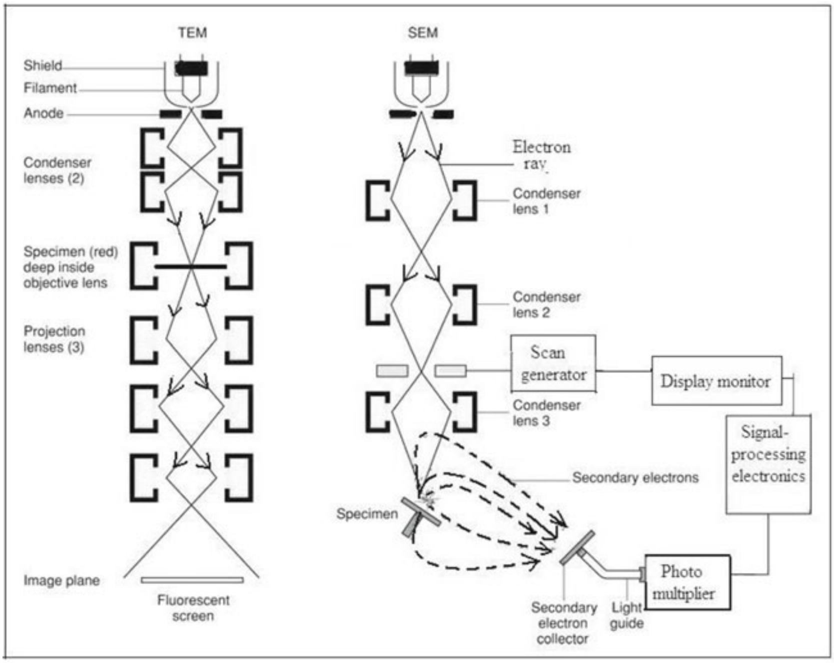

Fig. 6.21: TEM gives overall illumination and SEM gives point illumination.

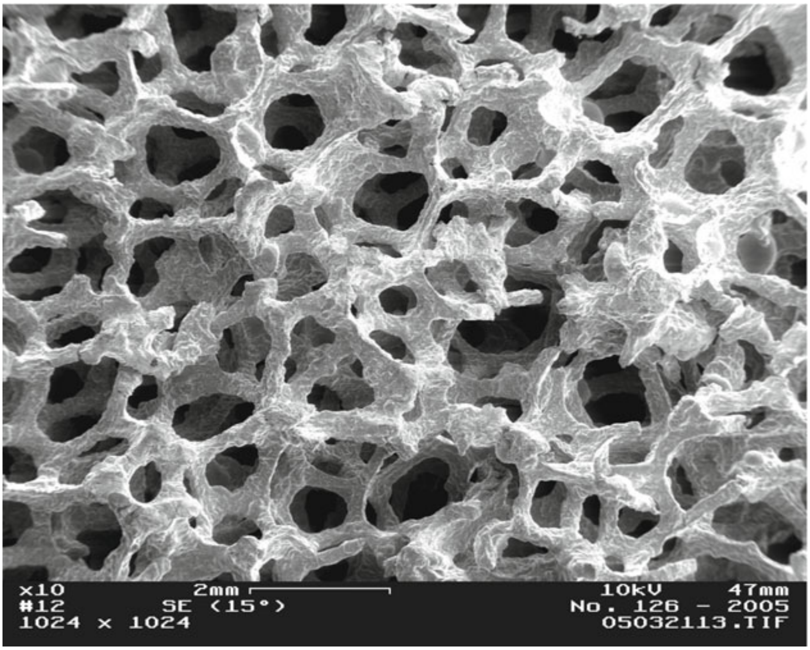

Fig. 6.22: Metal foam in scanning electron microscope.

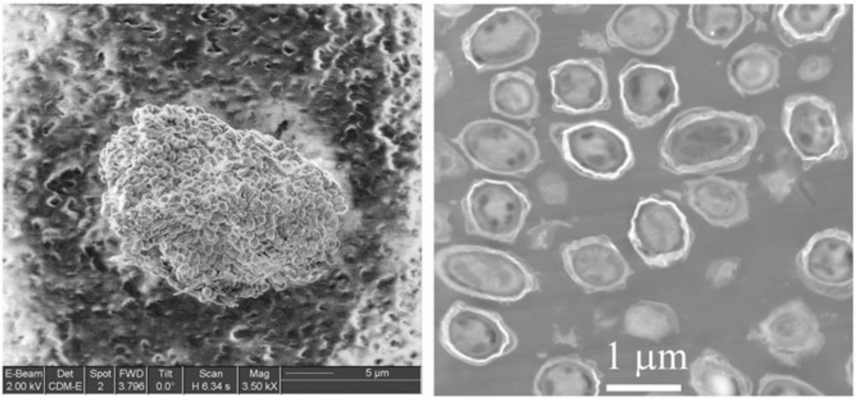

Fig. 6.23: Bacillus anthracis as viewed in scanning electron microscopy (left) and transmission electron microscopy (right).

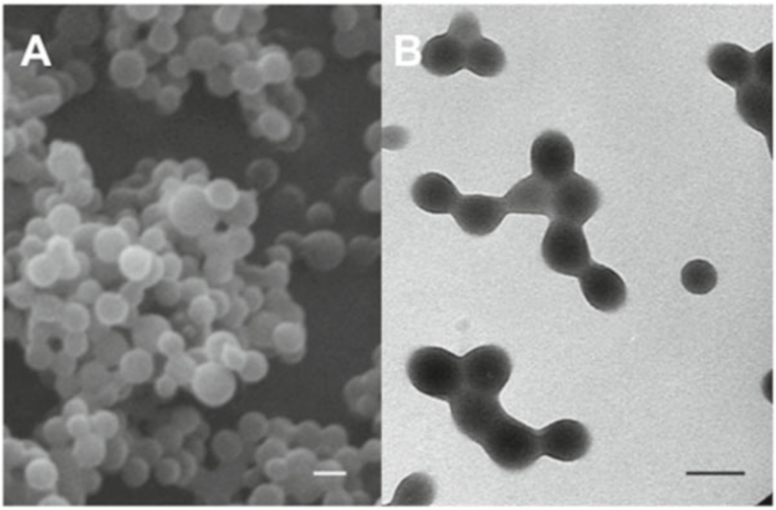

Fig. 6.24: Scanning electron microscope (A) and high resolution transmission electron microscope (B) images of PCL NPs.

Note: All scale bars shown in the figure are 150 nm. Abbreviations: NPs, nanoparticles; PCL, poly(ε-caprolactone).

6.7 APPLICATIONS OF ELECTRON MICROSCOPY

(i) Differentiating phases based on mean atomic number (related to relative density) using BSE.
(ii) Compositional map shows the variation of different trace elements.
(iii) High resolution image of the shape of the object is produced.
(iv) Very small feature of the object can be observed by using SEM.
(v) Crystallographic orientation and microfabric can be studied in detail by using the backscattered electron image.
(vi) The different phases can easily be distinguished by BSE image.

6.8 ELECTRON PROBE MICRO ANALYSER

This technique utilizes a highly focussed electron beam (5-30 keV) to probe the elemental composition of the sample. The electrons in the beam interact with the sample over a very minute area and excite the elements present there to produce their characteristic x-rays. These characteristic x-rays are recorded and the elements present in the sample can be identified using a Wavelength Dispersive XRF spectrometer (WDF). Both qualitative and quantitative analysis is possible with this non-destructive method, with ppm detection level and 1% reproducibility.

A schematic diagram of the experimental arrangement is shown in Fig. 6.25. Electron gun produces electrons from the low energy tungsten filament and then accelerated by a positively biased plate to 10-30 keV. The beam passes through central hole of the anode plate, then collimated (using suitable apertures) and focussed. The beam is focussed using a number of magnetic lenses (condensing coils) and allowed to fall in the sample. This sharply focussed high energy beam excites a volume of the sample as small as three micrometres. The x-rays thus produced are analyzed using a WDX spectrometer. This detecting system identifies the elements by detecting corresponding characteristic x-rays. Chemical composition is determined by comparing the intensity of each peak with the standards. Higher beam currents produce more x-rays from the sample and improve both the detection limits and accuracy of the resulting analysis. A transmitted light optical microscope is attached to the system for locating the study area with an accuracy of one micrometre.

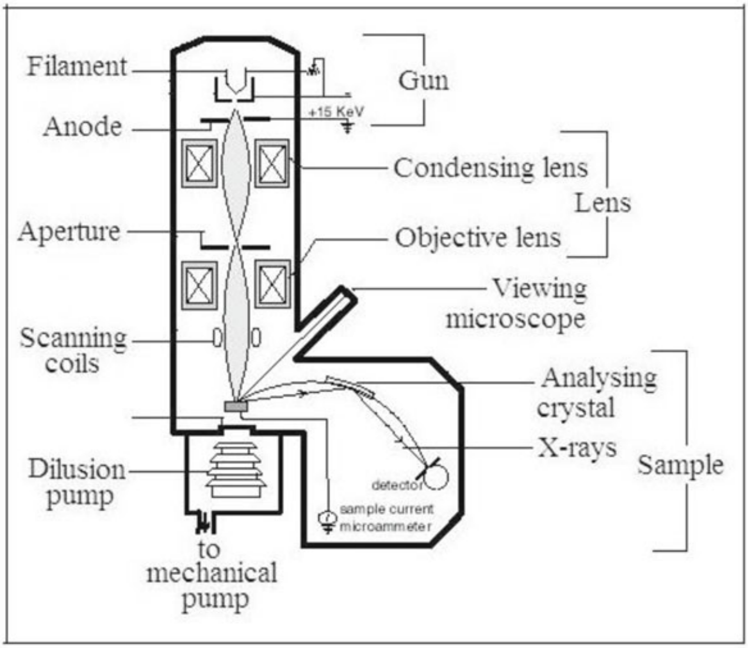

Fig. 6.25: A sketch of EPMA.

Using suitable detector, the following image analysis can be done:

1. Analysis of the images occurred from the secondary electrons (SEI), backscattered electrons (BSE) and cathode luminescence (CL).
2. Possible to take 2D elemental maps.
3. Using EDS and WDS, compositional information data collection is possible.
4. Analysis of crystal lattice preferred orientation (EBSD) is possible.

The electron microprobe can do quantitative analysis of samples for elements from fluorine ($Z = 9$) to uranium ($Z = 92$). This can determine elemental compositions in stratified layers of material from nm to mm thickness.

Major applications are in geochemistry, mineralogy, material science e.g. glass, ceramics, cement, microelectronics, physical metallurgy, nuclear metallurgy and biochemistry.

Advantages

(a) It is very useful for analyzing solid samples in a very small spot e.g. 1-2 micron diameter, and can identify a very minute single phase present.
(b) In situ analysis of very small compositional variations in a sample spot or chemically zoned material is possible.
(c) With the array of imaging detectors (SEI, BSE and CL) attached to microprobe, the surface and internal compositional study is possible.

Limitations

(a) Waters in the hydrous minerals cannot be analyzed and also unable to detect very light elements like Li, He etc.
(b) Microprobe analysis results as oxide of elements not as cations. Thus following stoichiometric rules, formula of the sample composition/mineral composition to be derived.
(c) Precaution must be taken for composite/overlapping peak analysis.
(d) Since probe is unable to distinguish valence states e.g. ferric/ferrous ratio, some complimentary technique (e.g. Mossbauer) to be used when needed.

6.9 IR SPECTROSCOPY

Infrared spectroscopy is used to study the chemical functional groups present in the sample and also the types of bond present. It allows exposing the sample with infrared radiation and studying its absorption spectra.

Natural vibrational frequencies of atoms in molecules and crystals fall in the infrared range and are quantized. Exposing the sample to infrared radiation, the absorbed energy causes enhanced vibrations of the molecules. Depending on the functional group present (i.e. the chemical bonds), the characteristic frequency is absorbed and the absorption spectra are obtained. Four different vibration modes are bending, rocking, twisting and scissoring as shown in Fig. 6.27.

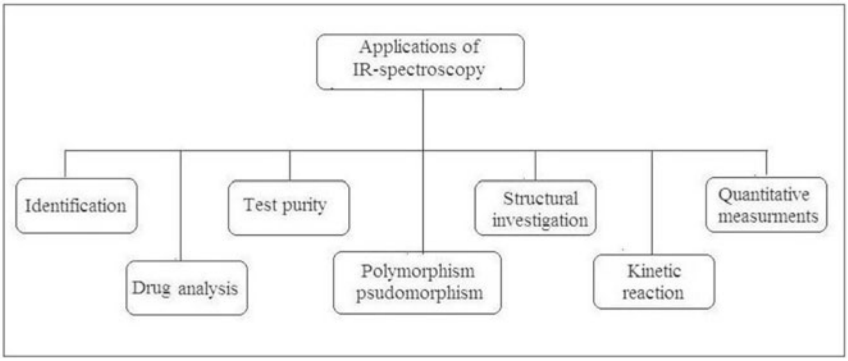

Fig. 6.26: Various applications of IR spectroscopy.

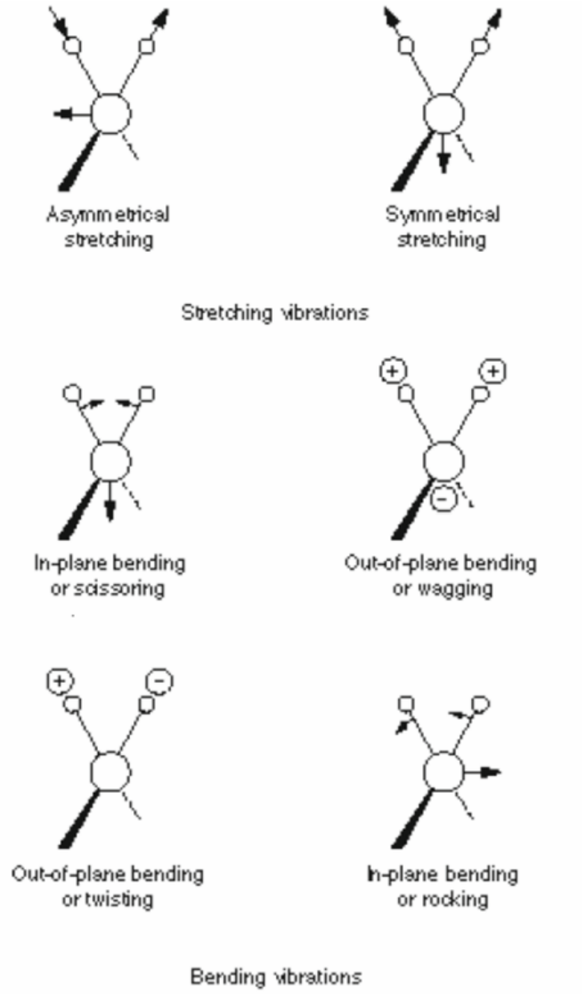

Fig. 6.27: Different vibration modes of molecules.

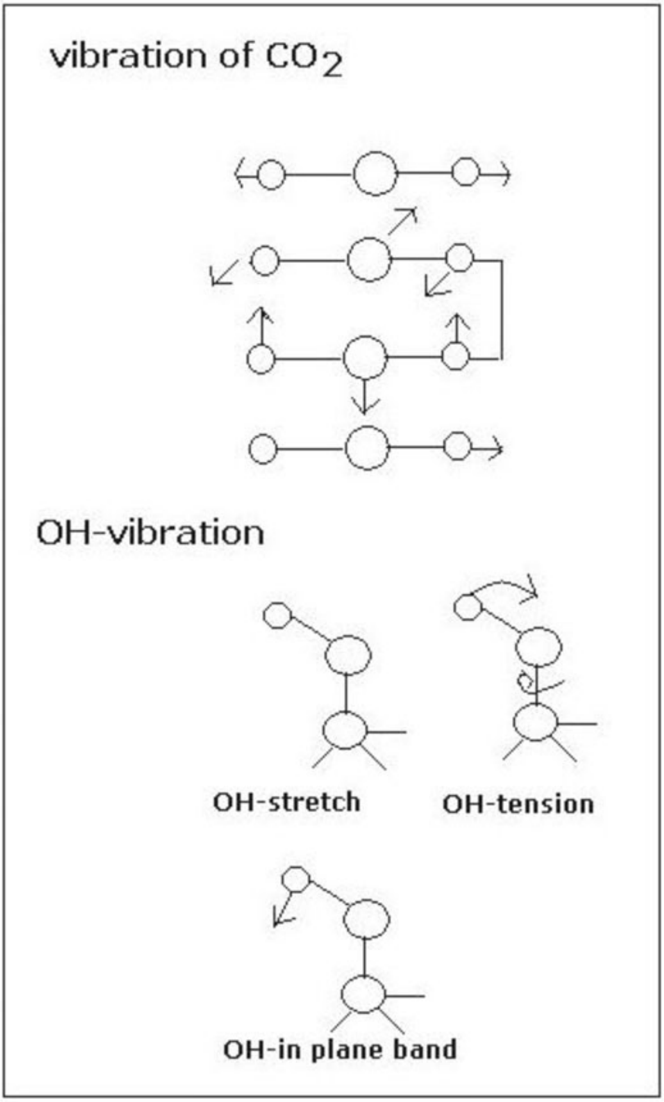

Fig. 6.28: Vibration modes of specific chemical groups.

Infrared frequencies fall between visible and radio waves and is divided in three ranges of wave number [ν (in cm^{-1}) = 1/λ (in μm)]

Near-Infrared
13000-4000 cm^{-1}, λ = 0.782.5 μm. Region with its higher energy level and higher frequencies can excite overtones or harmonic vibrations.

Medium Infrared
4000-200 cm^{-1}, λ = 2.5-50 μm may be used to study the fundamental vibrations and associated rotational vibrational structure.

Far Infrared

200-10 cm^{-1}, $\lambda = 50\text{-}1000\ \mu m$. The longer wavelength far-IR has lower energy and may be used for rotational spectroscopy.

Infrared absorption frequency depends on strength of bonds, mass of atoms and stretching or bending modes and vibrations.

IR analysis use absorbance and transmittance properties of the sample and defined as follows:

$$\text{The transmittance } T = \frac{\text{Power transmitted by the sample } (I)}{\text{Powder incident on the sample } (I_0)}$$

And the absorbance A is related as

$$A = \log_{10}(1/T) = -\log_{10} T = -\log_{10} I/I_0$$

The transmittance range is 0-100% whereas absorbance is from infinity to zero.

Collection of Output Information

A block diagram of the simplest analysis process is shown in Fig. 6.29 where output information is sequentially collected in time using a single detector by scanning each spectral element at a time. This simple instrument was modified using multiple detectors.

On further improvement, multiple devices are used with a single detector. The signals are then decoded for identifying in the spectral elements. A double beam IR-spectrometer is shown in Fig. 6.30. The incident beam is split into two and one is falling on the sample and another on the reference and compared. Commercially available reference materials are used.

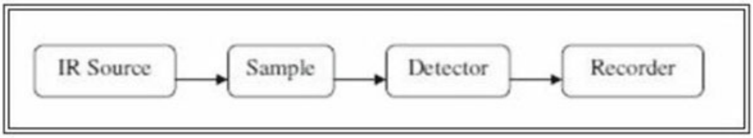

Fig. 6.29: Flow chart of IR data collection.

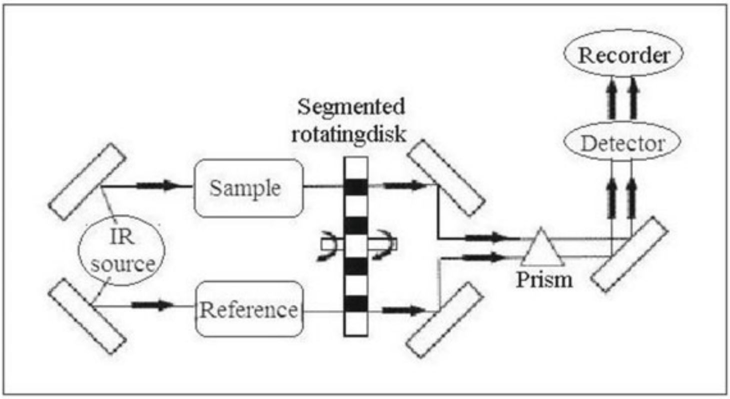

Fig. 6.30: Double beam IR-spectrometer.

There are many varieties of IR-spectrometers developed according to the need of experimental analysis. These are summarized in a sketch (Fig. 6.31).

Further improved version of the IR-spectrometers is the FTIR (Fourier Transformed IR) unit. FTIR method collects all wavelengths simultaneously and thus making the data collecting process very fast. The output data from the sample is collected using an interferometer and digitized in an interferogram. Fourier transform is then performed on the data to obtain the spectrum.

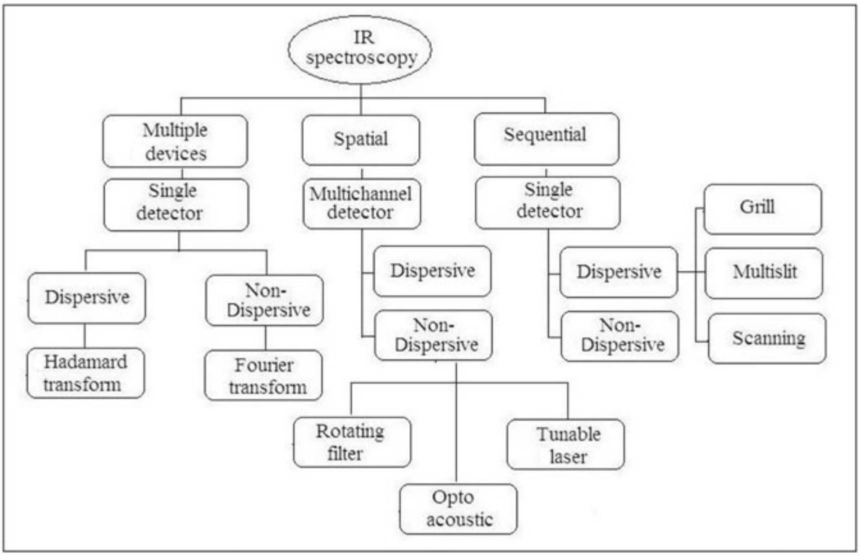

Fig. 6.31: Variations in IR spectrometry.

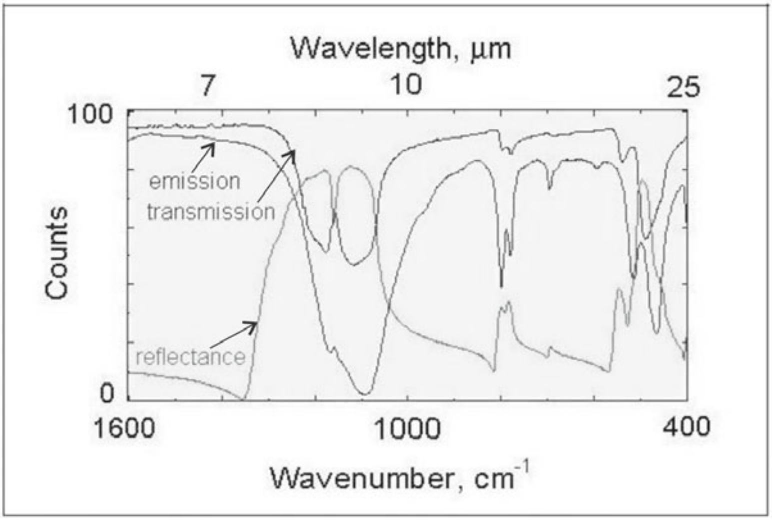

Fig. 6.32: Typical IR-spectra of quartz.

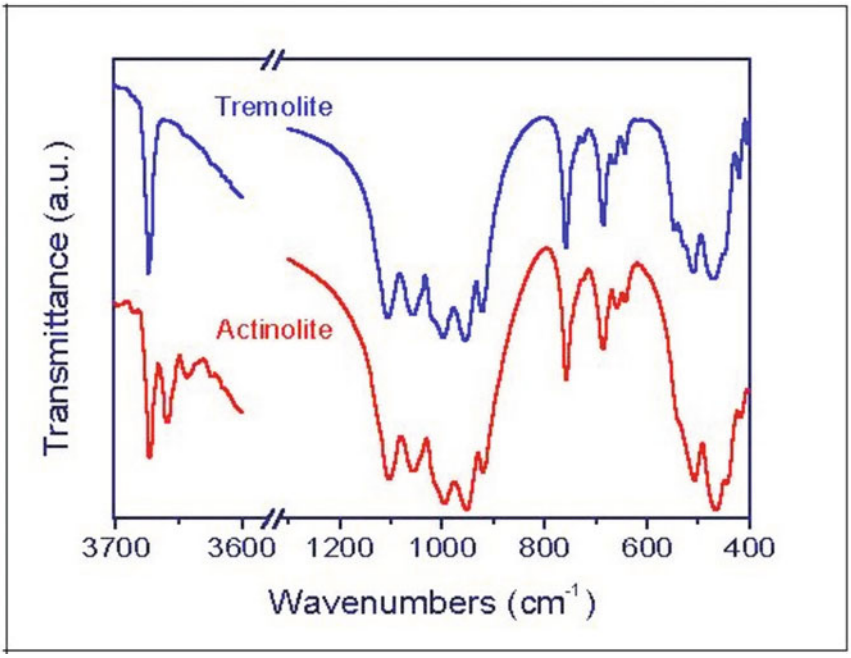

Fig. 6.33: Typical IR-spectra of trimolite-actinolite.

Analytical Technique

For inorganic compounds and minerals IR-wave length range generally from 0.2 to 50 µm. This technique can analyse solid, liquid and gaseous phases. Sample preparation methods are accordingly different. For solid samples, usual preparation process is to mix homogeneously grinded solid sample with KBr and make a pellet by pressing. For reflectance spectra, special attachments are necessary. For transmission spectra, the grain size of the sample must be around 20 µm and good absorption spectra needs finer particle size, around 5 µm. When the refractive index of the sample is nearing 1, transmission band wave length is more prominent. The peak positions shift with average particle size variation and should be considered during sample preparation. For molecules containing more than one chemically active group in their unit cell (e.g. CO_3 in calcite), vibrations in individual molecules couple with each other and frequency shift occurs resulting in band splitting. For such complicated interactions interpretations of IR-bands on solid samples are more difficult compared to the liquid or gaseous samples.

The sample is put to the sample position for analysis. In analysis of mixtures accuracy is 1% under optimum condition, and 5% for routine analysis. The points to be considered for good data are: (i) Molecules must be active in the IR-region. (ii) Minimum elemental information is given for most samples. (iii) In the required spectral region, transparent background matrix for solvent or solid is essential.

Comparing the spectra of unknown samples with the band of standard samples, identification is done. As the coordinated atomic bonds increase, possible rotational or vibrational modes will increase and also the wavelength range, e.g. for silicate minerals, wavelength range is 9-12 μm. Increased ratio of Si:O (isolated silica tetrahedral, like SiO_4 Olivine), the strong absorption range is 0.25 and in quartz (SiO_2) is 0.50. Hydroxyl group containing minerals (goethite, serpentine, lepidocrocite etc.) have their characteristic absorption band wavelengths greater than 2800 cm^{-1} and are due to the stretching vibrations within the hydroxyl group. This technique is thus able to characterise the types of bond present and can get the finger print of the sample under study.

6.10 RAMAN SPECTROSCOPIC ANALYSIS

Raman spectroscopy is an inelastic light scattering technique used to study the vibrational, rotational, and other low frequency modes in molecular system. In this method of chemical analysis, the sample is exposed to a beam of monochromatic light or a laser beam in the frequency range of visible, infrared or near-ultraviolet region. It is having wide applications in geochemistry, mineralogy and also organic and biological studies.

Raman effect is a scattering phenomenon where the photons incident on the sample are scattered with or without changing its energy. Major part of these photons are scattered without energy change and exhibit Rayleigh scattering phenomena. A small fraction of the photons, interacting with the molecular centres of the sample, have their energy altered to both high energy and low energy side. This is called Raman scattering and the scattered energy levels are known as stokes (on higher energy side) and anti-stokes (lower energy side) lines.

Raman spectroscopy measures the wavelength and intensity of the inelastically scattered light from molecules. Depending on the molecular vibration energy, the Raman scattered light is being shifted from the incident light. This is called *Raman shift* and measured in wave numbers (in cm^{-1}). For relation between wave length and wave numbers of shift in the Raman spectrum, the following formula can be used:

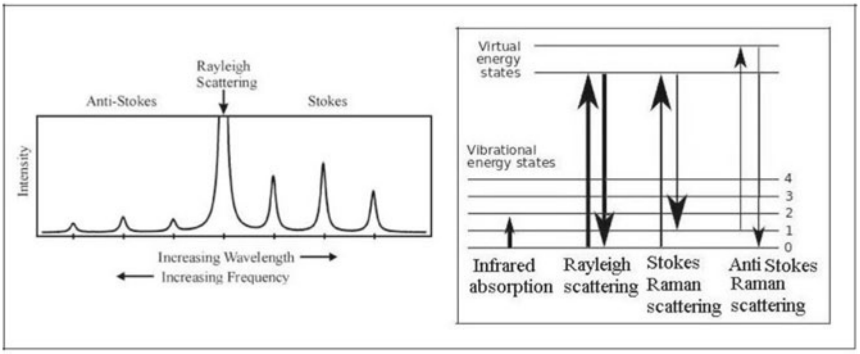

Fig. 6.34: Rayleigh and Raman scattering spectra.

$$\Delta\omega = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1}\right)$$

where $\Delta\omega$ is the Raman shift expressed in wave number, λ_0 = the excitation wavelength and λ_1 is the Raman spectrum wave length.

Most commonly, the units chosen for expressing wave number in Raman spectra is inverse centimetres (cm^{-1}). Since wave length is often expressed in units of nanometres (nm), the formula above can scale for this units conversion explicitly, giving

$$\Delta\omega\ (\mathrm{cm}^{-1}) = \left(\frac{1}{\lambda_0(\mathrm{nm})} - \frac{1}{\lambda_1(\mathrm{nm})}\right) \times 10^7,$$

effectively multiplying by $\frac{(\mathrm{nm})}{(\mathrm{cm})}$

The basic parts of Raman spectrometer are (i) excitation source, a laser beam, (ii) sample illumination system (usually an intense, polarized and coherent laser beam in the UV, visible, or near-infrared range) and light collection optics (collected with a lens and is sent through interference filter or spectrophotometer), (iii) wave length selector i.e. filter spectrophotometer and (iv) detector system.

In the experimental arrangement, the sample is exposed to laser beam of suitable energy and the scattered light is collected. The wave lengths of these scattered light yield information about the status of the chemical functional group and hence the bond features of the sample under study. This non-destructive technique can analyse solid, liquid and gaseous samples. Needed sample amount is about 10 mg and in some specific cases the amount is as low as 10 to 50 ng. Liquid samples can run in aqueous solutions.

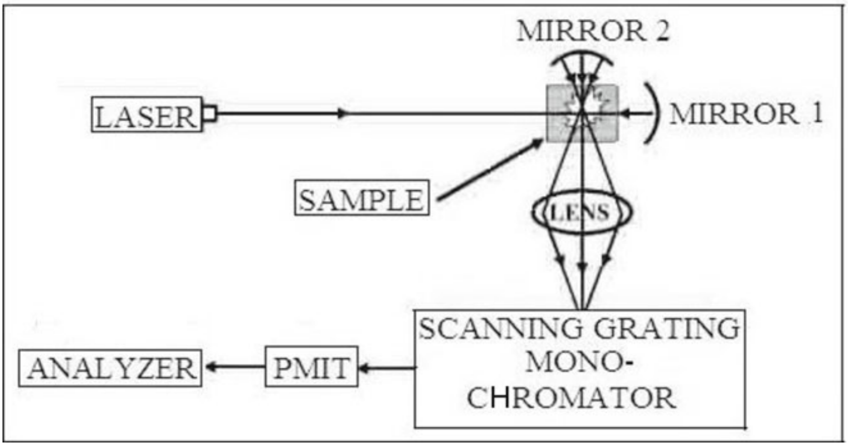

Fig. 6.35: A sketch of Raman spectrometer principle.

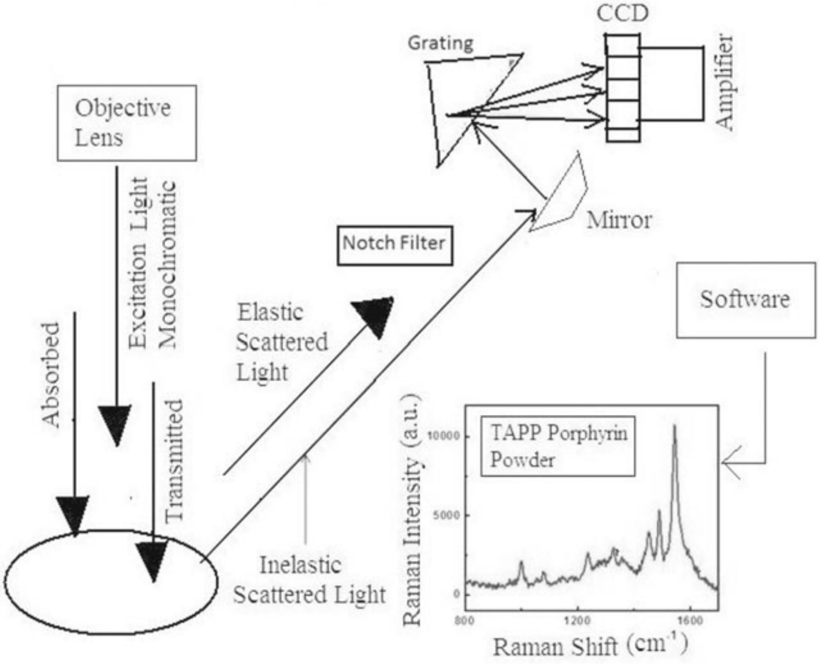

Fig. 6.36: Arrangement details (Notch filter to remove stray light) of a Raman Spectroscope.

Rayleigh scattering line is very strong compared to the Raman scattering lines. The stray lights of Rayleigh line are also of comparable (or a little stronger) intensity and also in the frequency range, close to the Raman lines. These stray lines are generated in the spectrometer during the light dispersion on gratings. This dispersion is reduced using a holographic gratings. The separation of these lines is a problem. Commercially available interference filters (notch) is used to cut off the spectral range close to the region where the effect of these stray lines are prominent.

6.11 TYPES OF RAMAN SPECTROSCOPE

For specific types of data, needed developments are incorporated in the Raman spectroscopic analysis. These are:

1. Surface Enhanced Raman Spectroscopy (SERS)
Enhances the Raman scattering by adsorbing molecules on rough metal surfaces (colloidal metals, e.g. gold/silver) and the enhancement factor may be of the order of 10^{11}.

2. Resonance Raman Spectroscopy (RRS)
To enhance the vibrational modes of the excited electronic states of a molecule or crystal, the excitation wavelength is matched accordingly. This is useful for studying large molecules.

3. Tip Enhanced Raman Spectroscopy (TERS)

In this method, Raman signals are enhanced using a metallic tip (usually silver or gold coated) in the vicinity of the molecules of interest. The spatial resolution is of the size of the tip (20-30 nm). This is a very useful method for bio analysis.

4. Polarized Raman Spectroscopy (PRS)

It studies the polarization of Raman scattered light using a polarized laser excitation and a polarization analyzer. The molecular orientation and vibrational symmetry information (relating to the molecular shape e.g. polymorph analysis, liquid crystal study etc.) can be obtained by this technique.

5. Spontaneous Raman Spectroscopy (SRS)

Variation of molecular behaviour with temperature variation is studied using this technique.

6. Transmission Raman Spectroscopy (TRS)

This is a very useful method for studying powder, capsules, living tissues etc. types of turbid materials in bulk. In medical diagnostic applications, this special method is of immense use.

7. Hyper Raman Spectroscopy (HRS)

When the second harmonics of the excited beam interact to the vibrational modes, the non-linear effects can be revealed which are normally not observed. This method depends on SERS type enhancement for analysis.

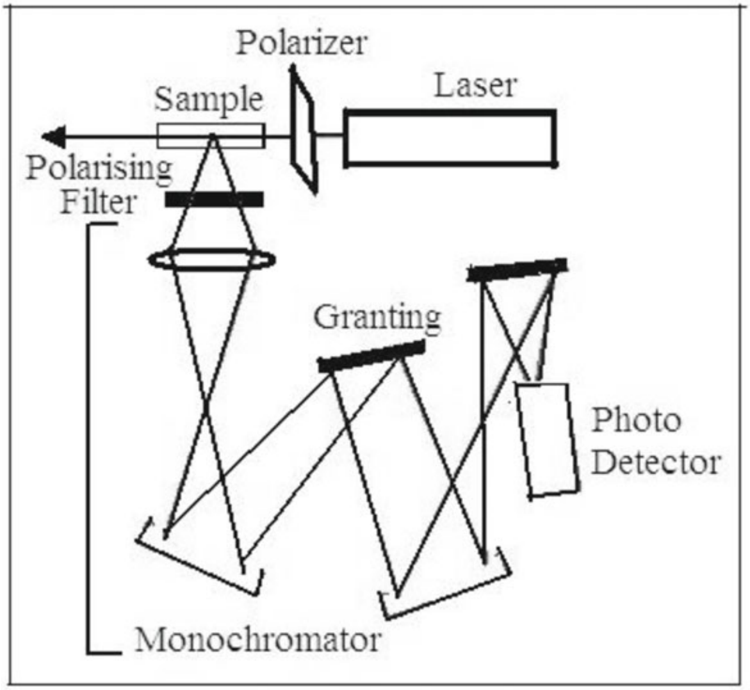

Fig. 6.37: A sketch of Raman spectrometer fitted with polarization facilities.

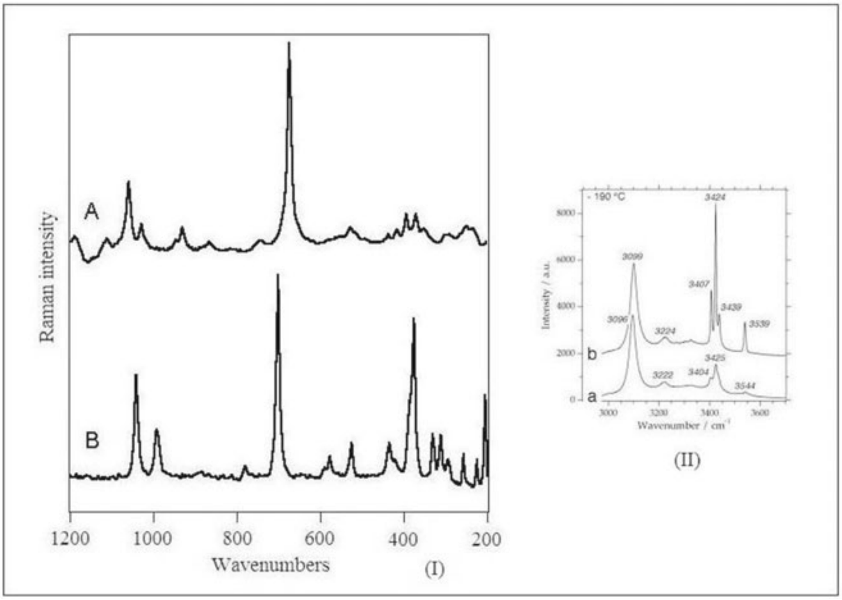

Fig. 6.38: (I): Raman spectra of (A) nephrite and (B) jadeite minerals. **(II):** Raman spectra of fluid and crystal mixtures in the systems H_2O, H_2O–NaCl.

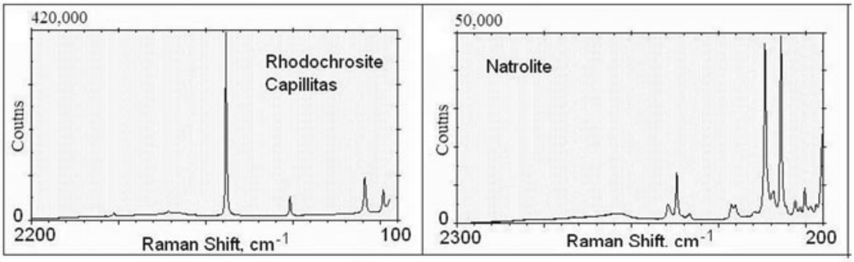

Fig. 6.39: Raman spectra of rhodochrosite and natrolite.

6.12 APPLICATIONS OF RAMAN SPECTROSCOPY

The major applications are:

1. Identification of functional groups in unknown substances in solids and aqueous solutions.
2. Identification of reaction components—Reaction kinetics study.
3. Detection of molecular impurities or additives.
4. Quantitative estimations of compounds in mixtures.
5. Non-destructive analysis of biochemical systems.
6. Surface studies using Surface enhanced Raman spectroscopy (SERS).
7. Studies of electronically excited molecular states.
8. Routine quality control analysis.

   And many more.

6.13 THERMAL ANALYSIS

Study of properties of materials with change in temperature is Thermal Analysis. Branches of thermal analysis are developed and named according to the study of various properties of the material. When on thermal treatment of a sample, heat is evolved, it is called *Exothermic* process and when heat is absorbed, known as *Endothermic* reaction. Possible processes of enthalpy changes and types of thermal reaction, i.e. exothermic or endothermic are listed in Table 6.4.

Table 6.4: Thermal effects corresponding to different reaction processes

Reaction process	Adsorption Catalytic reactions Crystallisation Polymerisation Curing	Desorption Melting Vapourisation Sublimation Desolvation (drying)	Solid-solid transition Solid-liquid reaction Solid-gas reaction Solid-solid reaction Decomposition
Observed effects	Exothermic	Endothermic	Exothermic and endothermic

Main applications of thermal analysis are: (1) Soil and clay analysis; (2) Determination of Glass transition; (3) Compositional effects on glass transition; (4) Heat capacity determination; (5) Characterization of polymer blends; (6) Study the effects of additives added to polymer; (7) Polymer degradation analysis; (8) Crystallinity and crystallization rate study; and (9) Reaction kinetic studies.

Different types of thermal analysis developed are on the basis of: (1) weight change, (2) energy change, (3) dimensional change and (4) evolved gas. They are grouped in Table 6.5.

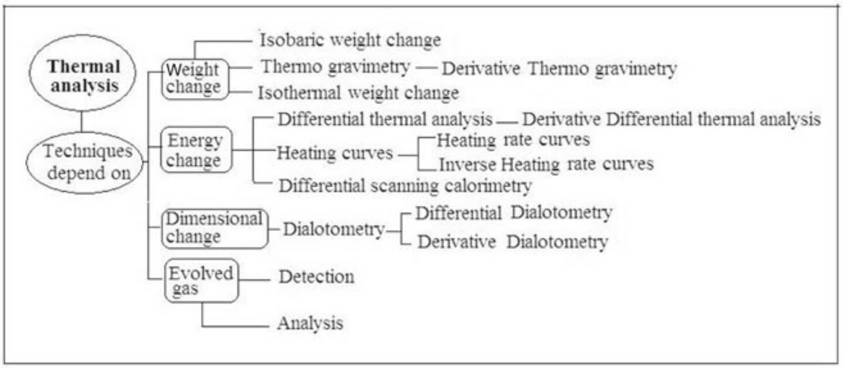

Fig. 6.40: Flow chart showing different types of thermal analysis.

Table 6.5: Different types of thermal analysis

Name of analysis	*Description*
Thermo gravimetric analysis (TGA)	Measures the change of weight of the sample with temperature variation.
Differential thermal analysis (DTA)	Measures the temperature differences in thermal reaction.
Differential scanning calorimetry (DSC)	Takes the data of heat difference in the thermal reaction under study.
Evolved gas analysis (EGA)	Studies the gaseous products under thermal decomposition.
Thermo mechanical analysis (TMA)	Is the study of dimension under thermal treatment.
Dynamic mechanical analysis (DMA)	Studies the mechanical stiffness and damping under thermal treatment.
Dilatometry (DIL)	Records the volume change in thermal reactions.
Thermo-optical analysis (TOA)	Is the study of thermal effects on change of optical properties.
Dielectric thermal analysis (DEA)	This is the study of dielectric permittivity and loss factor of the material under thermal reactions.

During thermal analysis, the main controlling parameters are sample heating rate, choices of gas for the needed environment and its flow rate, collection of evolved gas (for EGA) for further analysis. For each specific types of thermal analysis mentioned above, suitable accessories are needed for appropriate data collection.

A sketch for the basic instrument is shown in Fig. 6.41. It consists of two crucibles, one for the sample and other for the reference material (must be having steady thermal behaviour over the operating temperature range).

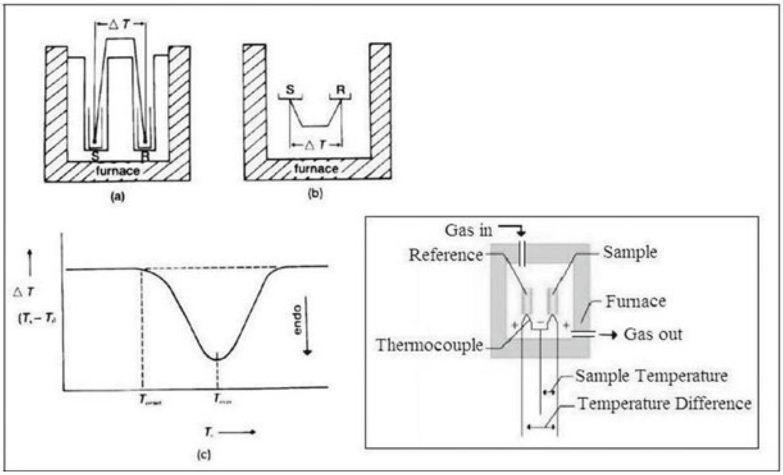

Fig. 6.41: Basic parts of a thermoanalyser.

Both the crucibles are attached to an electrically controlled heating arrangement. By changing the heater current, the heating rate can be controlled (mostly linear heating/cooling rate or stepwise isothermal measurements used). The temperatures of the sample and reference are measured by thermocouples attached to each crucible. In response to the change in the system properties (sample controlled thermal analysis), more advanced temperature controlling systems (oscillating in sine wave or square wave mode) is being developed and is known as Modulated Thermal Analysis.

Change in the weight of the sample during thermal treatment is recorded using electronic balance, attached to the crucibles. The whole set up is enclosed in a chamber with gas inlet and outlet for controlling the desired environment around the sample. According to the needed environment (atmosphere) of the experiment, measurements can be made using air (oxidizing atmosphere) or inert atmosphere using gases like nitrogen or helium and also may be used in suitable reducing atmosphere.

A separate arrangement may be provided for collecting evolved gas during thermal analysis, which may be used for further studies using some other suitable technique (may be using other relevant techniques like FTIR or mass spectrometry MS).

During thermal treatment, emission of light (electrical discharge from a dielectric material) or the mechanical relaxation (may be with the sound emission) in a stressed specimen can also be studied with the recorded time-temperature variation.

Thermal energy may be absorbed by causing structural changes in the sample. This heat transfer through structures is reflected in the sample's thermal conductivity or heat capacity and has many applications in engineering aspects of material science.

Thermogravimetric analyses measure the weight gain/loss with increasing temperature under inert or reactive environment. Each weight change corresponds to physical (i.e. crystallization, phase transformation etc.) or chemical (oxidation/reduction reactions) processes occurring with temperature change. For quantitative clay analysis in a mixture of clay minerals, TGA is a very effective method. Each clay phase is having its own decomposition temperature and from the corresponding weight loss data, each phase can be quantified. Differential scanning calorimetry (DSC) usually accompanies TGA and is used for calculating enthalpy energy changes or heat capacity changes associated with phase transitions.

An ideal DSC curve showing the change of heat flow process is in Fig. 6.42. Exothermic and endothermic peaks are marked as EX and EN. Due to the imbalance in the thermal capacities of the sample crucible, its contents etc., offset O is observed. The base line of the curve (B) is decided by the heat capacity of the sample. For a precise measurement, the baseline corrections can be made by comparing the empty and with the sample loaded pan data.

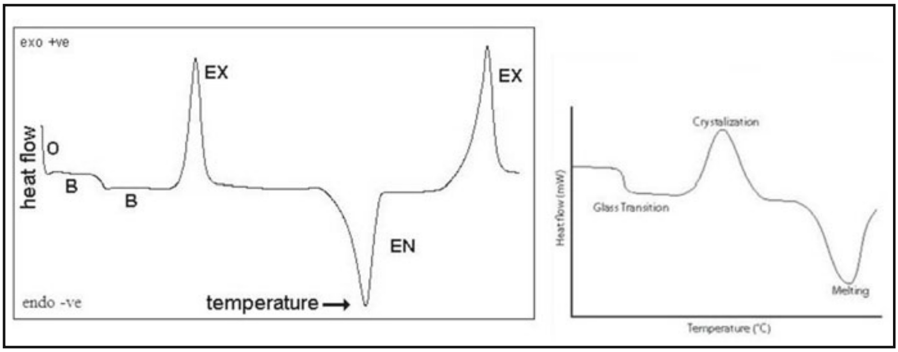

Fig. 6.42: Features of a DSC curve with a base line variation.

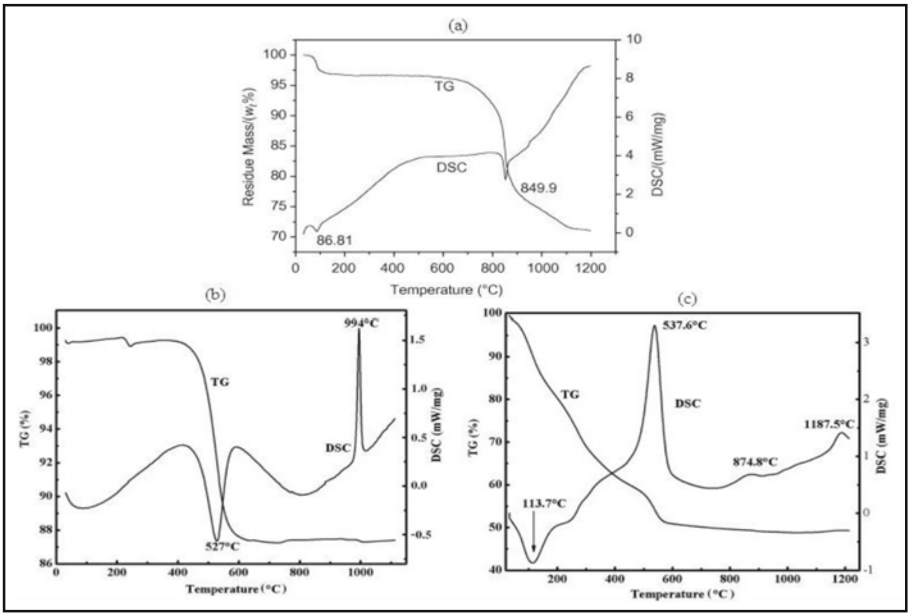

Fig. 6.43: (a) TG-DSC curves for K-feldspar; (b) TG-DSC curves for kaolinite; and (c) TG-DSC curves for Al (hydrous) oxide.

6.14 APPLICATIONS OF THERMAL ANALYSIS

1. Soil and clay analysis.
2. Determination of glass transition.
3. Compositional effects on glass transition.
4. Heat capacity determination.
5. Characterisation of polymer blends.
6. Study the effects of additives mixed with polymer.

7. Polymer degradation analysis.
8. Crystallinity and crystallization rate study.
9. Reaction kinetic studies.

Typical TG-DSC thermograms (simultaneous) are shown in Fig. 6.43. Peaks are yielding information by its position (e.g. temperature, start, end and extrapolated onset), size (depends on the amount on material and energy of reaction) and its shape related to the kinetics of the processes.

Concluding Remarks

For getting specific type of data to unfold the needed information the details of techniques described in this chapter helps to understand and choose a particular technique. For instance x-ray diffraction for internal structure analysis, XRF for elemental composition and XRD for crystal structure analysis, Mossbauer techniques for identification of iron valency state, thermal interaction analysis for decomposition/internal structure change.

QUESTIONS

1. Which technique is essential for clay mineral identification? Why? Can it identify more than one clay phase in a sample? What is the limitation of this technique?
2. For fast and non-destructive chemical composition (elements) analysis, name a suitable technique and explain the process with block diagram. What are the limitations?
3. Compare the difference of wavelength dispersive (WDX) and energy dispersive (EDX) XRF spectrum. In which other techniques these special dispersive spectrums are used?
4. In which technique, oxidation state can be identified? Explain the principle and its applications. What are the limitations?
5. Compare the difference of TEM and SEM and explain the principle and its applications.
6. Explain the process of identification of chemical groups (e.g., CO_3^-, $(OH)^-$ etc.) using infrared spectra.
7. How the elemental mapping is done with EPMA analyzer?
8. In the spectroscopic analysis, identify different techniques appropriate to energy range.
9. What are the different aspects of thermal analysis? Explain them with example.
10. In clay samples, more than one clay phases are detected using XRD. Is it possible to quantify them using some other technique?

11. Why the decomposition temperatures are different even when the chemical compositions are same, e.g. calcite and aragonite? How the heat energy is used when there is no gas emission (like CO_2 from CO_3 group or H_2O from OH^- group etc.)?

FURTHER READING

Adrian, Marc, Dubochet, Jacques, Lepault, Jean and McDowall, Alasdair W. (1984). Cryo-electron microscopy of viruses. *Nature*, **308(5954):** 32-36. Bibcode 1984Natur.308...32A. doi:10.1038/308032a0. PMID 6322001

Bailyn, M. (1994). A Survey of Thermodynamics. American Institute of Physics, New York. ISBN 0-88318-797-3.

Bearden, J.A. (1967). X-Ray Wavelengths. *Reviews of Modern Physics*, **39(1):** 78-124. Bibcode 1967RvMP...39...78B. doi:10.1103/RevModPhys.39.78.

Beattie, J.A. and Oppenheim, I. (1979). Principles of Thermodynamics. Elsevier Scientific Publishing Company, Amsterdam. 0–444–41806–7.

Beckhoff, B., Kanngießer, B., Langhoff, N., Wedell, R. and Wolff, H. (2006). Handbook of Practical X-Ray Fluorescence Analysis. Springer, ISBN 3-540-28603-9.

Bertin, E.P. (). Principles and Practice of X-ray Spectrometric Analysis. Kluwer Academic/Plenum Publishers, ISBN 0-306-30809-6.

Bradbury, Tom (2000). Meteorology and Flight: Pilot's Guide to Weather (Flying & Gliding). A & C Black. ISBN 0-7136-4226-2.

Bryan, G.H. (1907). Thermodynamics. An Introductory Treatise dealing mainly with First Principles and their Direct Applications. B.G. Teubner, Leipzig.

Buhrke, V.E., Jenkins, R. and Smith, D.K. (1998). A Practical Guide for the Preparation of Specimens for XRF and XRD Analysis. Wiley, ISBN 0-471-19458-1.

Chou, K.C. (1983). Identification of low-frequency modes in protein molecules. *Biochemical Journal*, **215:** 465-469.

Chou, K.C. (1984). Low-frequency vibration of DNA molecules. *Biochemical Journal*, **221:** 27-31.

Chou, K.C. (1989). Low-frequency resonance and cooperativity of hemoglobin. *Trends in Biochemical Sciences*, **14:** 212.

Cullity, B.D. (1978). Elements of X-ray diffraction. Addison Wesley, ISBN 0-201-01174-3.

David, W.I.F., Shankland, K., McCusker, L.B. and Ch. Baerlocher (eds) (2002). Structure determination from powder diffraction data. IUCr Monographs on crystallography.Oxford Science Publications, ISBN 0-19-850091-2.

Debye, P. (1915). Zerstreuung von Röntgenstrahlen. *Annalen der Physik*, **351(6):** 809. Bibcode 1915AnP...351..809D. doi:10.1002/andp.19153510606.

Demirdöven, N., Cheatum, C.M., Chung, H.S., Khalil, M., Knoester, J. and Tokmakoff, A. (2004). Two-dimensional infrared spectroscopy of antiparallel beta-sheet secondary structure. *Journal of the American Chemical Society*, **126(25):** 7981. doi:10.1021/ja049811j. PMID 15212548.

Drummy, Lawrence, F., Yang, Junyan and Martin, David C. (2004). Low-voltage electron microscopy of polymer and organic molecular thin films. *Ultramicroscopy*, **99(4):** 247-256. doi:10.1016/j.ultramic.2004.01.011. PMID 15149719.

Dugdale, J.S. (1998). Entropy and its Physical Interpretation. Taylor & Francis. ISBN 978-0-7484-0569-5.

Ellis, D.I. and Goodacre, R. (2006). Metabolic fingerprinting in disease diagnosis: Biomedical applications of infrared and Raman spectroscopy. *Analyst*, **131(8):** 875-885. Bibcode 2006Ana.131.875E. doi:10.1039/b602376m. PMID 17028718.

Erni, Rolf, Rossell, M.D., Kisielowski, C. and Dahmen, U. (2009). Atomic-Resolution Imaging with a Sub-50-pm Electron Probe. *Physical Review Letters*, **102(9):** 096101. Bibcode 2009PhRvL.102i6101E. doi:10.1103/PhysRevLett.102.096101. PMID 19392535.

Fraundorf, P. and Shuhan Lin (2004). Spiral powder overlays. *Microscopy and Microanalysis*, **10:** 1356–1357. doi:10.1017/S1431927604884034.

Gardiner, D.J. (1989). Practical Raman spectroscopy. Springer-Verlag. ISBN 978-0-387-50254-0.

Gibbs, J.W. (1875). Graphical Methods in the Thermodynamics of Fluids: Collected Works, Vol. 1, cited by Serrin, J. (ed.) (1986). An Outline of Thermodynamical Structure. *In:* New Perspectives in Thermodynamics. Springer, Berlin. ISBN 3-540-15931-2.

Halvorson, R.A. and Vikesland, P.J. (2010). Surface-Enhanced Raman Spectroscopy (SERS) for Environmental Analyses. *Environmental Science & Technology*, **44(20):** 7749-7755.

Hamm, P., Lim, M.H. and Hochstrasser, R.M. (1998). Structure of the amide I band of peptides measured by femtosecond nonlinear-infrared spectroscopy. *J. Phys. Chem.*, **B102(31):** 6123. doi:10.1021/jp9813286.

Harwood, Laurence M. and Christopher J. Moody (1989). Experimental organic chemistry: Principles and Practice (Illustrated ed.). Wiley-Blackwell. ISBN 0-632-02017-2.

Jansen, W. and Slaughter, M. (1982). Elemental mapping of minerals by electron microprobe (pdf). *American Mineralogist*, **67(5-6):** 521-533. http://www.minsocam.org/ammin/AM67/AM67_521.pdf.

Jenkins, R. (1999). X-ray Fluorescence Spectrometry. Wiley, ISBN 0-471-29942-1.

Jenkins, R. and De Vries, J.L. (1973). Practical X-ray Spectrometry. Springer-Verlag, ISBN 0-387-91029-8.

Jenkins, R., Gould, R.W. and Gedcke, D. (1995). Quantitative X-ray Spectrometry. Marcel Dekker, ISBN 0-8247-9554-7.

Kohli, K., Davies, Gordon, Vinh, N., West, D., Estreicher, S., Gregorkiewicz, T., Izeddin, I. and Itoh, K. (2006). Isotope Dependence of the Lifetime of the 1136-cm^{-1} Vibration of Oxygen in Silicon. *Physical Review Letters*, **96(22):** 225503. Bibcode 2006PhRvL..96v5503K. doi:10.1103/PhysRevLett.96.225503. PMID 16803320.

Kuo-Chen Chou (1988). Review: Low-frequency collective motion in biomacromolecules and its biological functions. *Biophysical Chemistry*, **30:** 3-48.

Kuo-Chen Chou and Nian-Yi Chen (1977). The biological functions of low-frequency phonons. *Scientia Sinica*, **20:** 447-457.

Landsberg, P.T. (1961). Thermodynamics with Quantum Statistical Illustrations. Interscience Publishers, New York.

Lau, W.S. (1999). Infrared characterization for microelectronics. World Scientific. ISBN 981-02-2352-8. http://books.google.com ?id=rotNlJDFJWsC& printsec =frontcover.

Liss, Klaus-Dieter, Bartels, Arno, Schreyer, Andreas and Clemens, Helmut (2003). High-Energy X-Rays: A tool for Advanced Bulk Investigations in Materials Science and Physics. *Textures and Microstructures*, **35(3-4):** 219. doi:10.1080/07303300310001634952.

Luft, J.H. (1961). Improvements in epoxy resin embedding methods. *The Journal of Biophysical and Biochemical Cytology* (Rockefeller Univ Press), **9(2):** 409. http://jcb.rupress.org/content/9/2/409.full.pdf.

Maxwell, J.C. (1872). Theory of Heat (Third edition). Longman's, Green & Co, London.

McMullan, D. (1993). Scanning Electron Microscopy, 1928–1965. 51st Annual Meeting of the Microscopy Society of America. Cincinnati, OH. http://www-g.eng.cam.ac.uk/125/achievements/mcmullan/mcm.htm. Retrieved 2010-01-31.

Mukamel, S. (2000). Multidimensional Fentosecond Correlation Spectroscopies of Electronic and Vibrational Excitations. *Annual Review of Physics and Chemistry*, **51(1):** 691. Bibcode 2000ARPC...51..691M. doi:10.1146 annurev.physchem.51.1.691. PMID 11031297.

Nebesáøovál, Jana and Vancová, Marie (2007). How to Observe Small Biological Objects in Low-Voltage Electron Microscope. *Microscopy and Microanalysis*, **13(3):** 248-249. doi:10.1017/S143192760708124X. http://journals.cambridge.org/abstract_S143192760708124X.

O'Keefe, M.A. and Allard, L.F. (pdf). Sub-Ångstrom Electron Microscopy for Sub-Ångstrom Nano-Metrology. Information Bridge: DOE Scientific and Technical Information – Sponsored by OSTI. http://www.osti.gov/bridge/servlets/purl/821768-E3YVgN/native/821768.pdf. Retrieved 2010-01-31.

Orr, P.J., Kearns, S.L. and Briggs, D.E.G. (2009). Elemental mapping of exceptionally preserved 'carbonaceous compression' fossils. *Palaeogeography Palaeoclimatology Palaeoecology*, **277 (1-2):** 1-8. doi:10.1016/j.palaeo. 2009.02.009

Padmanabha Rao, M.A. (2010). UV dominant optical emission newly detected from radioisotopes and XRF sources. *Brazilian Journal of Physics*, **40(1)**.

Paula, Peter and Atkins, Julio de (2009). Elements of physical chemistry (5th ed.). Oxford University Press, Oxford. ISBN 978-0-19-922672-6.

Planck, M. (1897/1903). Treatise on Thermodynamics. Translated by A. Ogg, Longmans, Green, London.

Planck, M. (1914). The Theory of Heat Radiation (Second edition). Translated into English by M. Masius. Blakiston's Son & Co., Philadelphia. Reprinted by Kessinger.

Ramos-Sánchez, M.C., Rey, F.J., Rodríguez, M.L., Martín-Gil, F.J. and Martín-Gil, J. (1988). DTG and DTA studies on typical sugars. *Themochim Acta*, **134:** 55-60.

Schlücker, S. et al. (2011). Design and synthesis of Raman reporter molecules for tissue imaging by immuno-SERS microscopy. *Journal of Biophotonics*, **4(6):** 453–463. doi: 10.1002/jbio.201000116.

Serrin, J. (Ed.) (1986). An Outline of Thermodynamical Structure. *In:* New Perspectives in Thermodynamics. Springer, Berlin. ISBN 3-540-15931-2.

Thomsen, J.S. (1962). A restatement of the zeroth law of thermodynamics. *Am. J. Phys.*, **30:** 294-296.

Urabe, H., Sugawara, Y., Ataka, M. and Rupprecht, A. (1998). Low-frequency Raman spectra of lysozyme crystals and oriented DNA films: Dynamics of crystal water. *Biophys J.*, **74:** 1533-1540.

Urabe, H., Tominaga, Y. and Kubota, K. (1983). Experimental evidence of collective vibrations in DNA double helix Raman spectroscopy. *Journal of Chemical Physics*, **78:** 5937-5939.

Van Grieken, R.E. and Markowicz, A.A. (2002). Handbook of X-Ray Spectrometry, 2nd ed. Marcel Dekker Inc., New York, Vol. 29, ISBN 0-8247-0600-5.

Warren, B.E. (1990). X-ray diffraction. Addison Wesley, Reading MA/Dover, Mineola NY, ISBN 0-486-66317-5.

Wittry, David B. (1958). Electron Probe Microanalyzer, US Patent No 2916621, Washington, DC: U.S. Patent and Trademark Office.

Zhang, X. and Briggs, D.E.G. (2007). The nature and significance of the appendages of Opabinia from the Middle Cambrian Burgess Shale. *Lethaia*, **40(2):** 161-173. doi:10.1111/j.1502-3931.2007.00013.x. http://www3.interscience.wiley.com/journal/117996987/abstract. Retrieved 2008-08-20.

PART II

Industrial Uses of Clays and Argilloids

CHAPTER

7

CLAYS: INDUSTRIAL APPLICATIONS AND THEIR DETERMINANTS

The applications of clays and their derivatives in the industries are many and varied. The suitability of a clay in a particular industry is determined by the properties of clay minerals present in it, which are in turn determined by the internal structures and chemical compositions of those clay minerals. General absence or scarcity of transition elements, which have strong pigmentation properties, facilitate the use of kaolinite-rich clays in production of high-quality porcelain. Owing to their distinctive structures, clay minerals exist with very fine grainsize and have high surface activity, and are therefore suitable as fillers in rubber industries. In addition to these properties, the whiteness of kaolinite makes it ideal filler in paper industry. Cation exchange property of some clay minerals, which is a result of their characteristic t–o–t–c layer structure, enables their use as filters and absorbents. The characteristic internal structure imparts to some clay minerals, esp. smectites, their distinctive lubricating and thixotropic properties, facilitating the use of bentonite clays in drilling fluids.

The easy availability of clays in almost all inhabitable places on earth and its certain characteristic properties facilitate its diverse use in the human civilisation since prehistoric time. The clays were widely used in building muddy huts or in the production of bricks, potteries etc. even in the most primitive forms of cultures. In the present age, the uses of clays and clay minerals are increasing day by day, and they are gradually replacing metals in various fields as cheaper, better and environment-friendly alternatives.

The diverse applications of clays and argilloids in the industries are elaborately described in the succeeding chapters of this Part. Clay is used in the industry in the following three forms:

- **Per se, with some beneficiations:** In the drilling fluids, absorbents and filters, clays can be directly used without any processing or alteration,

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though some beneficiation may be needed. These uses of clay are described in Chapters 8 and 12.

- **In chemically altered form with much processing:** Some kaolinite-rich clays are the **chief constituents** of the ceramics that include potteries, porcelain and refractory materials. In these industries the clays undergo intense processing and alteration, and are transformed irreversibly to different materials. These applications of clays are described in Chapter 9.
- **As one of the raw materials, in subsidiary proportions:** In rubber and paper industries, clays are not the chief constituents – they are used as fillers with the main constituents (cellulose, rubber etc.). In paint and medicine industries also, small proportions of clays are mixed with other substances. Clays are processed and altered as per the requirements of these industries. These uses of clay are described in Chapter 11.

In addition to the above uses of clays and clay minerals, some industrial applications of associated minerals are also described in this part. For example, the uses of phosphate compounds in fertilizer industries and manganese compounds in battery industries are described in Chapters 10 and 14 respectively.

The applicability of clay in a particular industry depends on the characteristic properties of the clay mineral(s) present in it. The properties of a clay mineral, on the other hand, depend largely on its internal structure and chemical composition. This chapter lays a foundation for the subsequent discussion and explains how the chemical composition and internal structure control some of the common industrial applications of clay minerals.

7.1 CERAMICS: POTTERIES, REFRACTORIES AND PORCELAIN

Clays are, by definition, plastic at appropriate water content and hard when fired. In plastic state the clays can be moulded into any shape, which produces a hard, coherent mass when dry, and a water-resistant, brick-like material when fired. *Ceramics* are the various kinds of hard, brittle, heat and corrosion-resistant materials produced by shaping wet clay, drying it and then firing it at a high temperature. Being hard and impervious, the ceramics are widely used in all types of potteries; while their high melting point and refractory (i.e. heat-resistant, stable at high temperature) properties facilitate their use in the production of fire bricks, for lining furnaces, crucibles etc.

When fired above a certain temperature, the clay is vitrified, i.e part of its components are molten to produce an impermeable glassy material. Vitrification generally takes place at about 1200°C – 1400°C, though different clay minerals may have different vitrification temperatures. *Earthenware* is porous, opaque and coarser ceramic that is fired below the vitrification temperature. It is opaque and its colour varies from light brown to reddish brown or darker shades of brown. *Porcelain* is the white translucent ceramic produced at higher than vitrification temperature. In contrast to earthenware, porcelain is much finer, having lower permeability, and greater hardness and toughness. Good quality porcelain is white, translucent and sonorous, with smooth, glassy surface.

For the production of high quality porcelain, the clay must be free of all colours. The transition elements, namely Ti, V, Cr, Mn, Fe, Co, Ni and Cu, have strong pigmentation properties. When present in the lattice of the clay mineral, they impart in it a characteristic colour and may also increase its opacity due to their greater absorption of light. Furthermore, when minerals of these transition elements are mechanically admixed with the clay as impurities, even in trace amounts, they can give a colour to the colourless clay mineral. In both ways, the transition elements render the clay useless in the manufacture of high quality porcelain.

Clay minerals of smectite and vermiculite groups contain Fe in octahedral sites, and sometimes other transition elements may also occupy this site replacing other cations. This imparts in the minerals green, yellow or brown tints, making them unsuitable in the production of high-quality porcelain. Illites may also show various pale shades. Kaolinite, on the other hand, has a general chemical formula of $Al_2 [Si_2O_5] (OH)_4$, and substitution of [Mg, Fe] for Al in the octahedral site is negligible (Table 7.1). Thus the clays predominantly composed of kaolinite, like primary and secondary kaolins and china clay, are most widely used for production of high-quality porcelain. But impurities containing transition elements, like hematite (Fe_2O_3), goethite (FeO[OH]), anatase (TiO_2), rutile (TiO_2) etc. may impart a colour to them. For this reason, many other kaolinite-rich clays like fire clay, common clay, refractory clay etc. are unsuitable in porcelain industry. These clays are used for lower quality ceramics, like refractory bricks, clay pipe, clay floor, wall tiles, drain tiles, sanitary wares etc. for which the white, translucent, glassy nature of porcelain is not needed.

Table 7.1. Proportions of transition element oxides in common types of clay minerals

Clay mineral species	*TiO_2 (%)*	*Fe_2O_3 (%)*	*FeO (%)*	*MnO (%)*
Kaolinite (Kaolinite group)	0.09	0.23	Nil	Nil
Illite (Illite group)	0.17	2.02	0.33	Nil
Montmorillonite (Smectite group)	0.06	3.19	Nil	0.03
Vermiculite (Vermiculite group)	Nil	8.01	Nil	Nil

Data obtained from Deer, Howie and Zussman (1992). The total quantity of transition elements is much less in kaolinite than other clay minerals.

7.2 FILLERS IN RUBBER INDUSTRIES

Rubber is a polymer with an empirical formula C_5H_8, along with 2–4% protein and 1–4% resins, fatty acids, and sterols. Like all polymers, the carbon and hydrogen atoms in the rubber are arranged in a definite array to form long chains. Fillers introduced in the inter-chain spaces (i.e. the space between the atomic chains) greatly modify the properties of the rubber, especially its strength, elasticity etc. In the manufacture of tyres, the fillers provide a large degree of strengthening to the rubber, resulting in a substantial increase in its stiffness, tensile strength, and resistance to abrasion. The fillers impart in the rubber higher breaking strength than unfilled rubber, consequently improving the longevity of the tyres in terms of overall load bearing, durability, and tread wear performance.

The properties of a material that determine its suitability as a filler and the properties it imparts to rubber are its grain-size, surface area of particles and surface activity of particles (i.e. the ability of the particle's surface to bond with the rubber matrix). These properties of clay minerals, especially kaolinite, and their appropriateness as fillers are explained below.

(a) **Grain-size:** If the size of the filler particle greatly exceeds the inter-chain space of the polymer, it introduces an area of localized stress and cannot strengthen the structure. Finer is the grain-size of the filler, greater will be the reinforcement provided by it to the structure. Kaolin, with grain-size 0.1-1 μm only, is therefore very much suitable as fillers and widely used in rubber industry.

(b) **Surface area of filler particles:** A filler must make intimate contact with the polymer chains in the rubber structure. Fillers that have a high surface area have more contact area available, and therefore have a higher potential to reinforce the rubber chains. Filler particles can be equidimensional (i.e. length, breadth and thickness are nearly equal, like cuboids or spheroids); platy (i.e. length and breadth much greater than thickness, like thin sheets) or acicular (i.e. needle-like shape, with length much greater than breadth and thickness). For a given grain-size, fillers with equidimensional particles have much less surface area than those with platy or acicular particle.

All clay minerals belong to the phyllosilicate subclass, having thin layers composed of successive tetrahedral and octahedral sheets of atoms and ions. The layers are weakly bonded to one another and thus easily separable to very thin flakes. The platy or flaky nature of the clay particles, thus having large surface areas relative to grain-size, is very much suitable to be used as fillers.

(c) **Surface activity of filler particles:** The filler particles must adhere strongly to the rubber matrix. Any gap or void not only decrease the strength of the structure considerably, but also increase its permeability and renders the rubber useless for many purposes. The surface chemistry of the filler determines how strongly it will adhere to the matrix of the rubber. Surfaces of clay particles are capable of forming hydrogen bonds with the constituents of rubber, and may also combine to the polymer chains as large anionic group through chemical reactions. The chemical reactivity of clay fillers in relation to the polymer chains of rubber can be improved with suitable surface coatings.

7.3 FILLERS AND COATINGS IN PAPER INDUSTRY

In the paper industry, fillers and surface coatings are applied for the following reasons:

(a) They increase the receptivity of ink on the paper surface, making the paper more suitable for printing and writing; and bring about sharp photographic illustrations and bright printed colours.
(b) They make the paper more suitable for reading also, by increasing its opacity. Reading is inconvenient on a translucent medium (like oiled paper).
(c) They make the paper surface whiter and smoother. Without any filler, the cellulose fibres on the paper surface appear coarse, dull with a yellowish tinge.
(d) They also increase the strength and stability of the paper.

Good quality fillers must be white and free of all colours, and have very fine grain-size so that its particles can settle easily in the interstices of cellulose fibres in the paper. In addition, it must disperse readily in water to produce a low viscosity fluid and adhere strongly to the cellulose fibres. Kaolinite is an ideal material to be used as filler for its whiteness [see Section 7.1], fine grain-size [see Section 7.2 (a)] and capabilities to adhere strongly [see Section 7.2(c)]. Furthermore, the thin plate-shaped particles of kaolinite are very soft and do not damage the cellulose fibres by abrasion during the manufacture of paper. Very low hardness and non-abrasiveness are characteristic properties of all clay minerals; resulting from the presence of loosely bound, easily separable structural layers in them. [see Section7.5 (d)].

7.4 FILTERS AND ABSORBENTS

Minerals of kaolinite group are composed of successive arrangement of parallel layers. Each layer contains one tetrahedral (t) and one octahedral (o) sheets of atoms and ions, therefore known as t–o layer. The t–o layers of kaolinites are electrically neutral, and bonded to one another by weak bond.

Illites, smectites and vermiculite, on the other hand, have trioctahedral or dioctahedral t–o–t layers, in which each octahedral sheet is sandwiched between two inward-pointing tetrahedral sheets. The substitution of Si^{+4} by Al^{+3} in the tetrahedral sites, and in some cases substitution of octahedral cations by cations of lower charge, produce charge imbalance in the t–o–t layers. That excess negative charge is balanced by a small number of *interlayer cations* that occur between two t–o–t layers, producing the characteristic t–o–t–c structure in these mineral groups. The most common interlayer cations are K^+ in illites, Ca^{+2} and Na^+ in smectites, and Mg^{+2} in vermiculite.

These interlayer cations may be readily replaced by other cations when the mineral surface is in contact with a liquid containing different types of cations like Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+} etc. This is known as *cation exchange* property of clay minerals. The cation exchange capacity is different in different types of clay minerals, as shown in table 7.2.

Table 7.2. Cation exchange capacities of different types of clay minerals.

Clay mineral group	*Cation exchange capacity (μeq/gm of clay)*
Kaolinite	10 May be up to 100 when impurities are present
Illite	200
Smectite	1000
Vermiculite	1000–1500

Data obtained from Deer et al. (1992) and Ghabru et al. (1989).

Tiller (1996) has concluded that the clay minerals have a stronger affinity for heavy metal cations than for alkali and alkaline earth cations. The clay minerals with high cation exchange capacity can thus be used in filters to remove heavy metal contaminants from the water.

In addition to the heavy metal cations, the interlayer spaces of smectites and vermiculite may also accommodate various organic molecules like glycol, glycerol, proteins etc. (Ravichandran and Sivasankar, 1997). The minerals of palygorskite-sepiolite group have tetrahedral sheets like the other phyllosilicates, but the cationic octahedra are linked together to form chains or ribbons, not the octahedral sheets. These octahedral chains are attached to the t-sheets, with much vacant spaces left in between them. Those vacant channels can also accommodate organic molecules. These clay minerals can therefore be used in the adsorbent and cleaning industries to remove harmful or unwanted organic molecules. Bentonite, which is largely composed of the smectite group mineral montmorillonite, is used for removing unwanted protein molecules from beer, juices and wines, thus improving their taste and quality.

Bleaching Earth is produced by acid treatment of bentonite. It has selective adsorption power, with high de-colouring rate and fast filtering speed. Its selective absorption power is utilised to adsorb toxins from fat and vegetable oils. Its decolouring and purifying properties facilitate its use in refining vegetable oils and animal fat, liquid glucose, maltose, sucrose etc. The removal of pigmenting substances from crude vegetable oils not only decolourizes them but also improves their taste and stability.

Fuller's earth, an argilloid containing palygorskite, sepiolite and some smectites, has been used for centuries to remove fat from animal wool (this process is known as *fulling*). Earlier, it was also used for oil refining before the industrial production of bleaching earth.

7.5 DRILLING FLUIDS

Drilling is carried out by rotating a drill bit under the weight of the metal pipes connecting the bit to the drilling rig. The metal pipes that are connected to drill bits and rotate with it are called drill strings. As the drill bit cuts into the rock, the *drill cuttings* (i.e. the particles of crushed sediments and rocks) are produced. The drill cuttings are removed from the bore hole by circulating a fluid of appropriate viscosity, density and other properties through it. That fluid is known as the *drilling fluid*. In addition to removal of the drill cuttings from the well, the drilling fluid also has the following functions:

- It lubricates the drill bit and drill string.
- The drill bit and drill string heats up by the friction with the rock it bores into. The drilling fluid cools them and cleans them during the drilling operation.
- The drilling fluid provides hydrostatic pressure to prevent ground water and other fluids from entering into the bore hole from the surrounding permeable rock formations.
- When the drilling operation is paused, the drilling fluid suspends the drill cuttings while the drilling assembly is brought in and out of the hole.

Drilling fluids are produced by adding fine particles of one or more selected solids to a liquid medium like water (water based drilling fluid) or oil (oil based drilling fluid). The solid particles are suspended in the liquid base and impart in the drilling fluid certain characteristic properties. When clays are added to sufficient quantity of water, a high density viscous fluid is produced. The density, viscosity and other properties of that fluid and its applicability as drilling fluids depend on the clay minerals and associated minerals present in the clay. Common water based drilling fluids are composed of water (76%), barite (15%), bentonite (7%) and 2% of other substances like salts, organic materials etc. (Web reference: Neff, 2005). In some cases palygorskite-sepiolite rich clays are used instead of or along with bentonite (Neff, o.c.).

Bentonite, which is largely composed of the smectite-group mineral montmorillonite, has the following functions in the drilling fluid.

(a) Barite ($BaSO_4$), a mineral of sulphide class having specific gravity 4.5, is added to the drilling fluid as weighing agent, i.e. to increase its density. Bentonite produces a highly viscous, thixotropic fluid when mixed to water, and thus acts as an ideal *viscosifier* in the drilling fluid. The high viscosity facilitates the easy suspension of barite particles in the drilling fluids, thus producing a high density fluid medium. The drill cuttings are easily suspended into this medium and removed from the bore hole.

(b) By increasing the viscosity of the drilling fluid, bentonite also slows down the rate of penetration of drilling fluid into the surrounding porous rock formations through the wall of the bore hole, thus preventing loss of drilling fluids.

(c) Being thixotropic, bentonite transforms the drilling fluid into a thick, gel-like material as soon as the drilling operation stops. That prevents the suspended drill cuttings and barite from settling and clogging the space in between the drill string and the borehole wall.

(d) An important function of bentonite in the drilling fluid is to lubricate the drill bit and the drill string, thus decreasing their friction with the wall of the bore hole. This function is attributable to the internal structure of montmorillonite of which the bentonite is composed. The t–o–t–c layers in the structure of montmorillonite are so weakly bonded to one another that they can easily slide past one another when even a little amount of force is applied. Like all clay minerals, montmorillonite is also very fine grained. Thus the fine-grained flakes of montmorillonite, which are easily separable to exceedingly thin sheets, produce a highly lubricating fluid when mixed with water.

(e) As a result of the characteristic internal structure explained above, montmorillonite is very soft and non-abrasive. Thus it does not abrade the drill bit and the drill string.

In addition to the above functions, the clay minerals used in the drilling fluid are environment-friendly. Being highly stable in the environment prevailing over or near the surface of the earth, they do not undergo any chemical alteration or release any pollutant or contaminant in the environment. This aspect of clay minerals is discussed in Section 17.6 (Part III).

Concluding Remarks

Clays have always been playing a significant role in the advent of human civilisation, and the socio-economic importance of clays and its derivatives increases day by day. The industrial growth and technological development of the contemporary age necessitates production of new materials, with new physical and chemical properties, to suit the latest needs. The prospects of synthesis of new, environment-friendly industrial substances from clays are widely explored by the technologists and material scientists throughout the world. A clear idea regarding the relation of internal structures of clay minerals, consequent physical and chemical properties of clays and their intended industrial applications is essential in such research and development activities.

QUESTIONS

1. Clays and their derivatives are now substituting metals in various fields. What do you think are the main economic and environmental advantages of this substitution?
2. Read the following section carefully:
   Electrons of inner shells in an atom/ion are in a lower energy level than those in the outer shells. Light passing through a mineral is absorbed when its energy of radiation corresponds to the difference in energy level of an inner electron and some higher orbital, and the inner electron is transferred to the latter. When that electron falls back to its original energy level, the absorbed energy is radiated. Some of the radiated energy may be in the visible spectrum.
   Now study from any book of U.G. level general chemistry the atomic structure of transition elements and explain why they have strong pigmentation property.
3. Is it justified to use the terms *ceramics* and *porcelain* interchangeably? Explain with reasons.
4. Consult Table 7.1 and explain why kaolinite is more suitable than smectite and vermiculite in the production of high quality porcelain.
5. Crude clay pots, widely used in rural India, are produced by moulding pots of common clay and firing them at low temperature. The water kept in them in summer is colder than the high quality porcelain pots. Why?
6. Which properties of clay minerals facilitate their use in the production of insulators?
7. Explain why clay minerals are suitable as fillers in rubber and paper industries.
8. Is it possible to substitute kaolinite with fine-grained, colourless quartz in the paper industry? Justify your answer.
9. Explain why the cation exchange capacity of vermiculite is much greater than that of kaolinite.
10. How does the role of bentonite in the drilling fluids differ from that of barite? Can any clay mineral substitute barite in the drilling fluid? Explain with reasons.

FURTHER READING

Carraher, C.E. Jr. (2000). Seymour/Carraher's Polymer Chemistry. 5th ed. (revised). Marcel Dekker, New York.

Clem, A.G. and Doehler, R.W. (1963). Industrial applications of bentonite. *In*: Swine ford Ada (ed). Clays and clay minerals. Proceedings of the Tenth National Conference on Clays and Clay Minerals, Austin Texas. Macmillan, New York.

Darley, H.C.H. and Gray, G.R. (1988). Composition and properties of drilling and completion fluids. 5th ed. Gulf Professional Publishing.

Deer, W.A., Howie, R.A. and Zussman, J. (1992). An introduction to the rock forming minerals. English Language Book Society with Longman.

Ghabru, S.K., Mermut, A.R. and St. Arnaud, D.R.J. (1989). Layer-charge and cation-exchange characteristics of Vermiculite (weathered biotite) isolated from a gray luvisol in northeastern saskatchewan. *Clays and Clay Minerals*, **37(2):** 164-172.

Harvey, C.C. and Lagaly, G. (2006). Conventional applications. *In*: Handbook of Clay Science. Bergaya, F., Theng, B.K.G. and Lagaly, G. (eds). Elsevier Ltd.

Jones, T.R. (1983). The properties and uses of clays which swell in organic solvents. *Clay Minerals,* **18:** 399 – 410.

Murray, H. H. (1963). Industrial applications of kaolin. *In*: Swine ford Ada (Ed). Clays and clay minerals. Proceedings of the Tenth National Conference on Clays and Clay Minerals, Austin Texas. Macmillan, New York.

Ralph, E. Grim (1962). Applied Clay Mineralogy. McGraw-Hill, New York.

Rankine, B. (1995). Making Good Wine: A Manual of Winemaking Practices for Australia and New Zealand. Sun Books, Melbourne.

Ravichandran, J. and Sivasankar, B. (1997). Properties and catalytic activity of acid-modified montmorillonite and vermiculite. *Clays and Clay Minerals,* **45:** 854–858.

Sarmento, M.R., Oliveira, J.C. and Boulton, R.B. (2000). Selection of low swelling materials for protein adsorption from white wines. *International Journal of Food Science and Technology,* **35:** 41–47.

Tiller, K.G. (1996). Soil contamination issues: Past, present and future, a personal perspective. *In*: Naidu, R., Kookana, R.S., Oliver, D.P., Rogers, S. and McLaughlin, M.J. (eds.). Contaminants and the Soil Environment in the Australasia-Pacific Region. Kluwer, Dordrecht.

Web References

Chemistry Encyclopedia, http://www.chemistryexplained.com/Ru-Sp/Rubber.html, last visited 26th June 2012.

Drill cuttings, http://www.irccm.org/coramm/drillcuttings.htm, © 2007 www.irccm.org, last visited 27th June 2012.

Neff, J.M. (2005). Composition, environmental fates, and biological effect of water-based drilling muds and cuttings discharged to the marine environment: A synthesis and annotated bibliography. Submitted to Petroleum Environmental Research Forum (PERF). http://perf.org/pdf/APIPERFreport.pdf, last visited: 29th June 2012.

Non-Black Fillers for Rubber, http://www.rtvanderbilt.com/NonBlackFillers.pdf, last visited 26th June 2012.

CHAPTER

8

TRADITIONAL AND MODERN USES OF CERAMICS, GLASS AND REFRACTORIES

Ceramics

8.1 INTRODUCTION

The word “ceramic” comes from the Greek word “keramikos”, “of pottery” or “for pottery.” A ceramic is an inorganic, non-metallic often crystalline oxide, nitride or carbide material made by the action of heat and subsequent cooling. During the heating and cooling non-crystalline ceramics also can be formed.

Table 8.1: Types of ceramics

Crystalline ceramics	*Non-crystalline ceramics*
Crystalline ceramic materials are not amenable to a great range of processing. Methods for dealing with them tend to fall into one of two categories – Ceramic forming techniques include shaping by hand (sometimes including a rotation process called “throwing”), slip casting, injection moulding, dry pressing etc.	Non-crystalline ceramics, being glasses, tend to be formed from melts. The glass is shaped when either fully molten or when in a state of toffee-like viscosity. If later, heat treatments cause this glass to become partly crystalline, the resulting material is known as a glass-ceramic.

Some elements such as carbon and silicon may be considered as ceramics. Traditional ceramic raw materials include clay minerals such as kaolinite, whereas more recent materials include aluminium oxide, known as alumina and also include silicon carbide and tungsten carbide. Ceramic materials are brittle, hard, and strong in compression, weak in shearing and tension. They

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withstand chemical erosion that occurs in other materials subjected to acidic or caustic environments. Ceramics generally can withstand very high temperatures, such as temperatures that range from 1000 °C to 1600 °C. It may be crystalline or partly crystalline and also may be amorphous. Though most common ceramics are crystalline. Many different ceramic materials are now used in domestic, industrial and building products. Clay was one of the earliest materials used to produce ceramics. Pottery objects, made from clay, were the earliest ceramics and hardened in fire. Later ceramics were glazed and fired to create a coloured, smooth surface. Ceramics now include domestic, industrial and building products. In the 20th century, new ceramic materials were developed for use in advanced ceramic engineering.

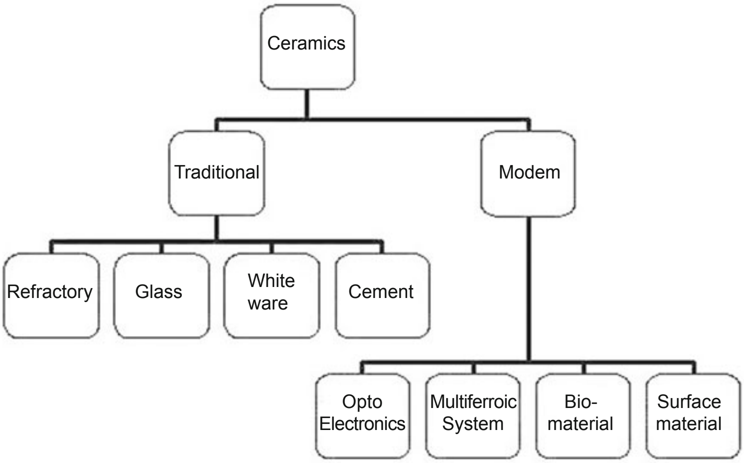

Fig. 8.1: Variation in ceramics.

8.2 PROPERTIES OF CERAMICS

The physical properties of any ceramic substance are a direct result of its crystalline structure and chemical composition. Density variations, grain-size distribution, type of porosity and second-phase content, can all be correlated with ceramic properties. Physical properties of chemical compounds include odour, colour, volume, density (mass/volume), melting point, boiling point, heat capacity, physical form at room temperature (solid, liquid or gas), hardness, porosity, and index of refraction. The microstructure includes most grains, secondary phases, grain boundaries, pores, micro-cracks, structural defects and hardness. Most bulk mechanical, optical, thermal, electrical and magnetic properties are significantly affected by the observed microstructure. The fabrication method is generally indicated by the microstructure.

8.3 MECHANICAL PROPERTIES

Mechanical properties include the many properties used to describe the strength of materials such as: elasticity, plasticity, tensile strength, compressive strength, shear strength and hardness. Fracture mechanics is concerned with the study of the formation and subsequent propagation of micro cracks in materials. In modern materials science, fracture mechanics is an important tool in improving the mechanical performance of materials and components. It applies the physics of stress and strain, in particular the theories of elasticity and plasticity. Thus, since cracks and other microstructural defects can lower the strength of a structure beyond that which might be predicted by the theory of crystalline objects, a different property of the material—above and beyond conventional strength—is needed to describe the fracture resistance of engineering materials. Fracture toughness is a property which describes the ability of a material containing a crack to resist fracture, and is one of the most important properties of any material for virtually all design applications. Fracture toughness is a quantitative way of expressing a material's resistance to brittle fracture when a crack is present. If a material has a large value of fracture toughness it will probably undergo ductile fracture. Brittle fracture is very characteristic of materials with a low fracture toughness value. Ceramic materials are usually ionic or covalent bonded materials, and can be crystalline or amorphous. A material held together by either type of bond will tend to fracture before any plastic deformation takes place, which results in poor toughness in these materials. These materials tend to be porous; the pores and other microscopic imperfections act as stress concentrators, decreasing the toughness further, and reducing the tensile strength.

Table 8.2: Electrical properties of ceramics

Electrical properties	*Description*
Semiconductivity	Some ceramics are semiconductors. Most of these are transition metal oxides, such as zinc oxide. Ceramicists are most interested in the electrical properties that show grain boundary effects. Semiconducting ceramics are also employed as gas sensors. When various gases are passed over a polycrystalline ceramic, its electrical resistance changes. With tuning to the possible gas mixtures, very inexpensive devices can be produced.
Superconductivity	The Meissner effect is demonstrated by levitating a magnet above a cuprate superconductor, which is cooled by liquid nitrogen. Under some conditions, such as extremely low temperature, some ceramics exhibit high temperature superconductivity. The exact reason for this is not known, but there are two major families of superconducting ceramics.
Piezoelectricity	A link between electrical and mechanical response is exhibited by a large number of ceramic materials, including the quartz used to measure time in watches and other electronics. The unit of time measured is the natural interval required for electricity to be converted into mechanical energy and back again.

(*Contd.*)

Table 8.2: (*Contd.*)

Electrical properties	*Description*
Pyroelectricity	The piezoelectric effect is generally stronger in materials that also exhibit pyroelectricity, and all pyroelectric materials are also piezoelectric. These materials can be used to inter-convert between thermal, mechanical and electrical energy; for instance, after synthesis in a furnace, a pyroelectric crystal allowed to cool under no applied stress generally builds up a static charge of thousands of volts.
Ferroelectricity	In turn, pyroelectricity is seen most strongly in materials which also display the ferroelectricity, in which a stable electric dipole can be oriented or reversed by applying an electrostatic field. Pyroelectricity is also a necessary consequence of ferroelectricity.

8.4 UN-FIRED AND FIRED PROPERTIES

Many un-fired and fired properties are the result of interaction of two or more key characterizing features. Figure 8.2 identifies these features for a traditional ceramics and shows their relation to properties that can be evaluated before and after firing.

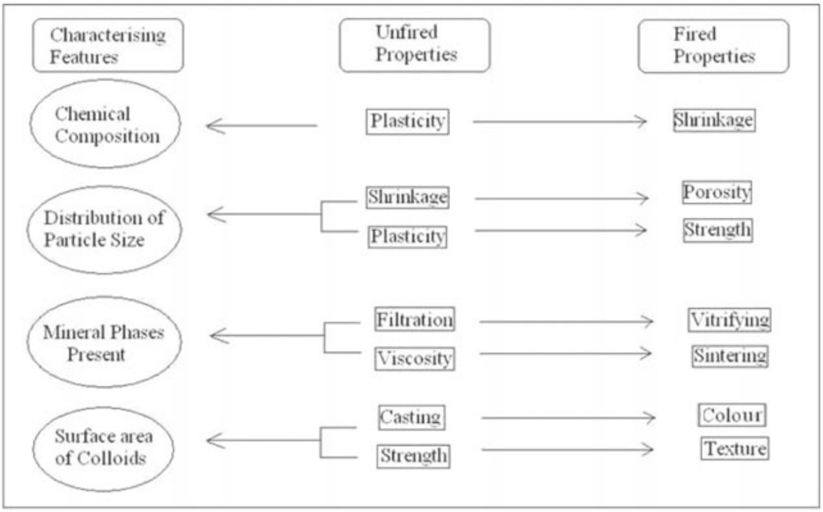

Fig. 8.2: Characteristic features of traditional ceramic and the properties that can be measured in un-fired and fired states.

8.5 OPTICAL PROPERTIES

Many ceramic substances, particularly the oxides, are optically transparent in single crystal or vitreous forms, e.g. the transparency of glass is perhaps its most useful and most characteristic feature. Optical properties are closely related to structure and composition of ceramics since the degree of polarization is a function of ion size, bounding energy and crystallographic direction. The index of refraction is a sensitive quantitative measure of these materials, parameters. Optically transparent materials focus on the response of a material to incoming light waves of a range of wavelengths. Material is characterized by its transparency in certain wavelength regions (% transmission/mm thickness). Many ceramics and most glasses absorb highly in the infrared and ultraviolet regions of the spectrum. Frequency selective optical filters can be utilized to alter or enhance the brightness and contrast of a digital image. Guided lightwave transmission via frequency selective waveguides involves the emerging field of fibre optics and the ability of certain glassy compositions as a transmission medium for a range of frequencies simultaneously (multi-mode optical fibre) with little or no interference between competing wavelengths or frequencies.

Large ions in crystals or in glass compositions are more readily polarised than small ones and produce a high index of refraction. Most glasses are in the range 1.4-2.0; metals are usually >3.0.

Table 8.3: Refractive index of various crystal phase

Crystal phase	*Refractive index*	*Crystal phase*	*Refractive index*
MgO	1.74	TiO_2	2.71
Al_2O_3	1.76	SiC	2.68
SiO_2	1.55	$BaTiO_3$	2.40
$ZrSiO_4$	1.95	LiF	1.392

8.6 DEVELOPMENT OF ADVANCED CERAMICS USING MODERN TECHNIQUES

On the basis of atomic, electronic, grain boundary, microstructure, and macrostructure, advanced ceramics have been developed. The interactions of these structural levels result in materials which have properties suitable for specific application. The successors require an in-depth knowledge and use of thermodynamics, kinetics, phase equilibria and crystal structure.

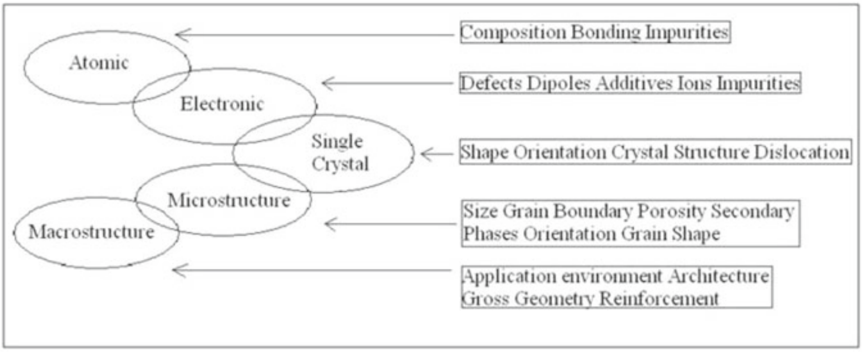

Fig. 8.3: Structural levels and interactions of ceramic materials.

8.7 USE OF CERAMICS

Ceramics differ from some other materials (viz. metals, plastics, wood products, textiles) in a number of individual properties, but perhaps the most distinctive difference to a designer or potential user of ceramic ware is the particularity of the individual ceramic piece. Actually ceramics are not readily shaped or worked after firing, except for some simple shapes of limited sizes. Many ceramics are manufactured as standard items: refractory bricks and shapes, crucibles, furnace tubes, insulators, thermocouple protection tube, fibre tubes etc.

Table 8.4a: Traditional use: Ceramic whiteware classes and their products

Class	*Types*	*Products*
Earthenware	Natural	Tableware, tiles
	Fine	Artware, kitchenware
	Talc	Artware, ovenware
Stoneware	Natural	Drain pipe, artware, kitchenware
	Fine	Tableware, cookware
	Basalt	Artware
	Jasper	Artware
Technical Ceramics	Electrical porcelains	Low-frequency insulators
	Steatite	High-frequency insulators
China	Cookware	Ovenware, stoveware
	Bone	Artware, tableware
Porcelain	High strength electrical	Low-frequency insulators
	Dental	Dentures
	Hard	Tableware, artware
	Technical vitreous	Ball mill ware, chemical ware

Table 8.4b: Use of ceramic products replacing metal items

Ceramics for replacing metal items	*Specific application*
Knife blades	The blade of a ceramic knife will stay sharp for much longer than that of a steel knife, although it is more brittle and can be snapped by dropping it on a hard surface.
Vehicle ceramic Brake discs	These are resistant to abrasion at high temperatures.
Advanced composite ceramic	They have been designed for most modern armoured fighting vehicles.
Ceramic balls	These can be used to replace steel in ball bearings. They are much less susceptible to wear and can offer more than triple lifetimes. They also deform less under load. In very high speed applications, heat from friction during rolling can cause problems for metal bearings, which are *reduced* by the use of ceramics. Ceramics are also more chemically resistant and can be used in wet environments where steel bearings would rust.

(*Contd.*)

Table 8.4b: (*Contd.*)

High-tech ceramic	It is used in watch making for producing watch cases, due to its light weight, scratch resistance, durability and smooth touch.
Ceramic gas turbine engines	Turbine engines made with ceramics could operate more efficiently, giving aircraft greater range and payload for a set amount of fuel (saves fuel).

8.8 BIOCERAMICS

Bioceramics, important subset of biomaterials, are ceramic materials that are biocompatible ranging from the ceramic oxides to the other extreme of resorbable materials. Bioceramics are used in many types of medical procedures. In primary medical procedures they are used as implants. Some rigid materials are commonly used as surgical implants though some bioceramics are flexible. Bioceramics are closely related to either the body's own materials, or are extremely durable metal oxides. In the medical fields as dental, and bone implants, ceramics are now commonly used. Artificial teeth and bones are relatively common place of its application. Surgical cements are used regularly. Joint replacements are commonly coated with bioceramic. Pacemakers, kidney dialysis machines, and respirators are the other examples of medical uses of bioceramics. Bioceramic materials are commonly subdivided by their bioactivity, viz. (i) Bioinert (ii) Bioactive. Bioinert includes oxide ceramics, silica ceramics, carbon fibre and synthetic diamond. Bioactive includes hydrogen apatite. Bioinert materials are non-toxic, non-inflammation causing. These materials must be long lasting, structural failure resistant, and corrosion resistant.

Table 8.4c: Advance ceramics: Applications of Bioceramics

Materials used	*Specific application*
Al_2O_3	Orthopaedic loadbearing applications
Surface active glasses	Dental implants
Glass-ceramics	Coating for chemical bonding
Al_2O_3, HA-autogenous bone composite	Alveolar ridge augmentations
Trisodium phosphate, calcium and phosphate salts	Temporary bone space fillers
Al_2O_3, HA, glass-ceramics	Otolaryngological applications
Al_2O_3, HA, HA-PLA composites, surface active glasses	Maxillofacial reconstruction
Al_2O_3	Coatings for tissues intergrowth
Bioactive glass-ceramics	Percutaneous access devices
PLA-carbon fibre composites	Artificial tendons and ligaments
Al_2O_3, HA-PLA composites	Periodontal pocket obliteration

Table 8.5: Products of clay-based ceramic materials

Ceramic materials	*Structural building materials*	*Refractory materials*	*Non-structural products*	*Structural products*	*Earthen ware*	*Stone ware*	*Porcelain*	*Technical ceramics*
Products	Bricks, terra cotta, roofing tiles	Flue lining, insulating bricks	Acid-resistant bricks, cement-clinker	Split bricks, quarry tiles	Pottery verified ware, table ware	Sanitary ware, tiles, insulators	Table ware	Chemical ware refractory ware

8.9 CLASSIFICATION OF CLAY-BASED CERAMICS

In modern science, ceramic is used in various aspects. Besides this ceramics developed on the basis of clay have some special uses such as structural building materials, refractory materials, non-structural products, structural products, earthen ware, stone ware, porcelain, and technical ceramics. The products of ceramic materials are known to us as bricks, terra cotta, flue lining, cement-clinker, chemical ware, refractory ware, table ware, tiles, sanitary ware, insulators, split bricks, quarry tiles, acid-resistant bricks etc.

The ceramics are classified into two types: coarse particles and fine particles. Again coarse particles are subdivided into porous and dense, on the basis of wt%, if weight % is greater than six then it will be defined as porous and if less than six it will be dense. Similarly fine particles are also subdivided into porous (weight % greater than 2) and (weight % less than 2) dense. The division porous again is classified in two types viz. structural building materials and refractory materials. Nonstructural products and structural products are the two subdivisions of dense or coarse particles. Earthenware is the example of the sub-division porous under fine particles. Dense is classified into three types, viz. stoneware, porcelain and technical ceramics.

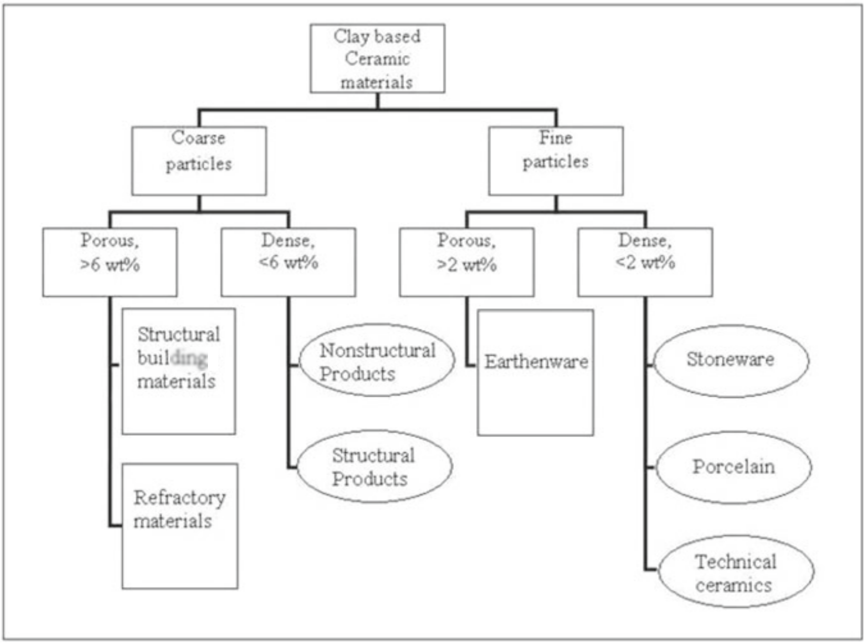

Fig. 8.4: Classification of clay-based ceramics.

8.10 CERAMIC PROCESSING METHOD

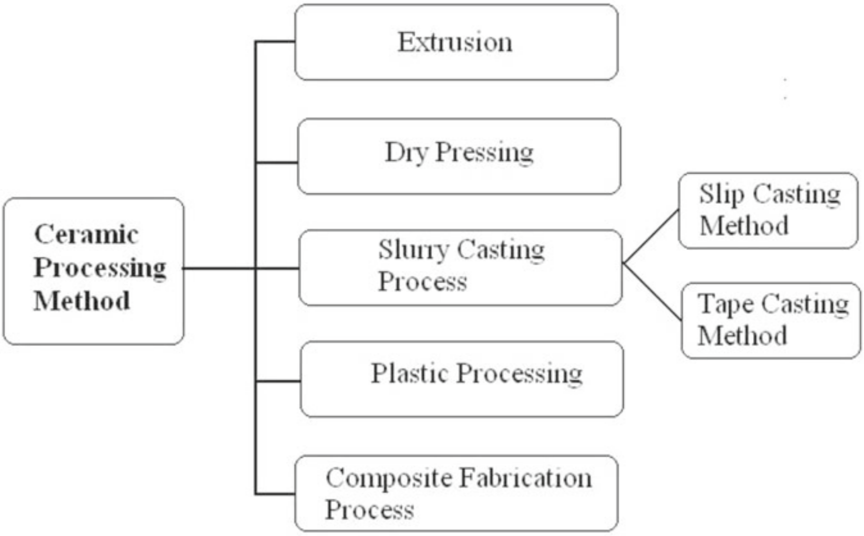

Fig. 8.5: Types of ceramic processing method.

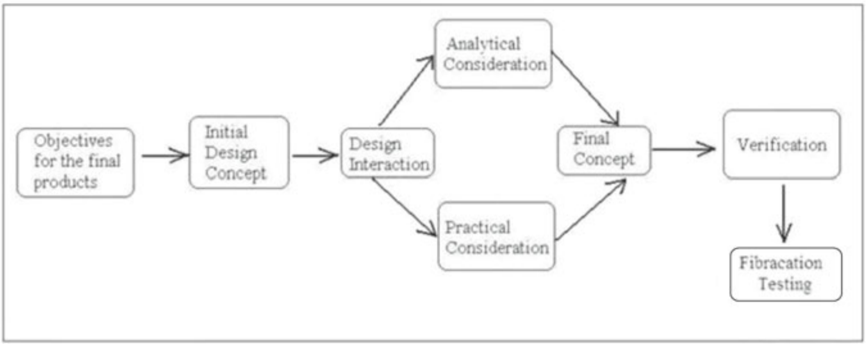

Fig. 8.6: Flow chart for ceramic design.

Ceramic processing occurs through some sequential activities, which starts with raw materials, proceeds through batch preparation and forming and concludes with firing. The sequence of steps is illustrated by Fig. 8.7. Ceramics are formed from raw materials used for traditional ceramics which are different from those used for advanced ceramics. For traditional ceramics raw materials consist of silica, clay, fluxes and are refractory materials. Silica is obtained either from massive quartz deposit or pure quartz sands. The quartz is washed and ground. The most commonly used clay minerals are kaolin and talc. China clay is predominantly kaolin. Ball clays are finer particle size clays that contain significant amounts of free silica and organic materials. Fluxes are materials, such as feldspars or nepheline syenite, which contain alkali oxides to promote the fusion of silica and alumina to form a glassy phase during firing. Refractory materials are a separate type of raw materials of ceramics and include oxides, carbides and other materials. It can easily withstand extremely high temperatures. Raw materials for advanced ceramics are usually chemically prepared powders of high purity. Powders of aluminum oxide, silicon nitride, zirconium oxide and silicon carbide are examples of highly processed raw materials for advanced ceramics. The optimum particle size distribution for ceramic powders is still a controversial issue. Fine spherical particles about 100 nm diameters is best for ordered packing into dense beds by highly dilute settling and are highly reactive.

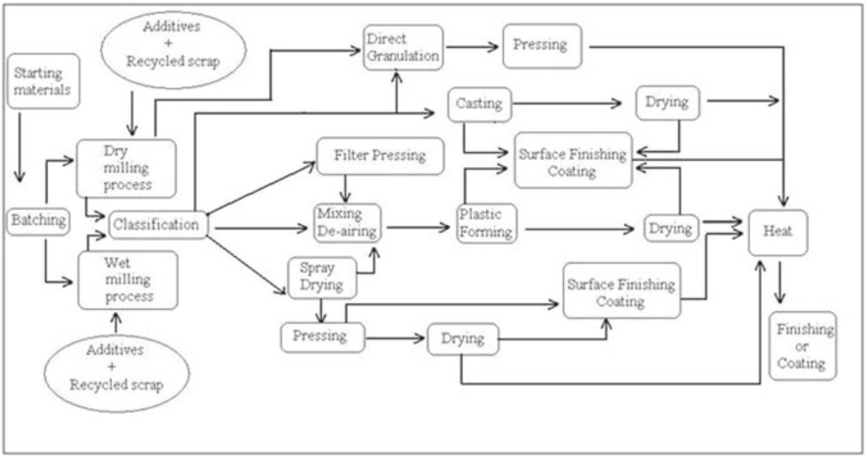

Fig. 8.7: General ceramic processing flow chart.

The powdered raw materials are prepared into various states that are compatible with the forming process. Powders used in dry processing methods are usually spray dried prior to pressing. The spray drying preparation permits the uniform incorporation of additives, such as binder and lubricants. Because spray drying is a granulation process, it combines many sub-micrometre sized powder particles into larger spherical particles that have excellent flow properties. Powders used in either slip casting or tape casting must be dispersed in aqueous or non-aqueous media to develop a fluid slurry. The proper dispersion of ceramic particles requires a thorough understanding of rheology and colloid chemistry. Dispersant type and amount, solids fraction, pH level and both powder particle size and distribution are important parameters. Ceramic powders used in either extrusion or injection moulding must be prepared.

Wide ranges of forming processes are used. Extrusion, dry processes and injection moulding are three processes that are widely used in polymer, metal and food technologies and therefore familiar to maximum engineers. Both slip and tape casting of ceramic slurries are process developed for ceramic materials. Forming process of a particular component or structure depends on many parameters viz. size, shape and volume of component.

Extrusion

The extrusion process for forming ceramics is widely used in the structural clay products industry and is used to a lesser extent in the white ware and refractories industries. The principle advantage of this method is rapid and economic formation of dense ware. Extrusion can be used for ware of any shape that has an axis normal to a fixed cross section. The cross section may contain holes produced by pins in the die through which the material is extruded. Extrusion usually comprises three stages: pugging, deairing and extrusion through a die. The dry material is fed continuously into one end of a long trough, spread with water and cut and kneaded by rotating knives into a homogeneous plastic mass. The plastic material is forced by an auger through a shredding die and into the deairing chamber in which a vacuum is maintained. Removal of air from the material improves extrusion characteristics and permits formation of denser ware.

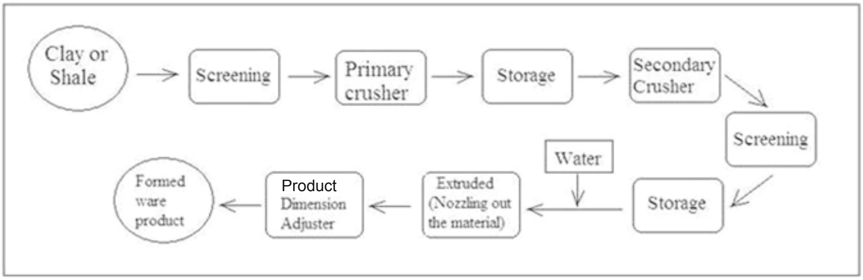

Fig. 8.8: Extrusion of structural clay bricks.

Table 8.6: Factors influencing forming process

Forming process	*Production value*	*Component shape*	*Component size*
Dry pressing	Small to medium	Simple	High
Injection moulding	Small	Complex	High
Slip casting	Large	Complex	Low
Tape casting	Thin sheets	Simple	High

Dry Pressing

It is a forming process in which nearly dry, free-flowing powders fill a metal die and are compacted under high pressure to the desired shape. Dry pressing process is more efficient. Shapes with a high aspect ratio, such as long, cylindrical bar are not prepared well by dry pressing because die well friction precludes the exertion of uniform pressure by the punches. The use of lubricant, both internal and external, to the ceramic powder reduces friction during the pressing process, facilitating forming and further reducing undesirable density variations. When very low density is required in the passed component or when the component shape is too complex, isostatic pressing is used in place of dry pressing. Traditionally, ceramic powder is placed in a rubber mould of the proper shape and sealed. Due to pressure, powder is compacted and yields uniform density. Currently it is more common in production to use dry bag.

Plastic Processes

The forming of ceramic shapes by deformation of plastic mass has been popular due to the highly plastic nature of clay-based traditional plastic body. Presently many traditional ceramic shapes are made by various plastic processes. The principal processes used are extrusion, injection moulding, plastic pressing etc. extrusion and injection mouldings are similar processes. Both processes are capable of rapidly forming ceramic shapes by compressing plastic raw feed either into a desired shape (extrusion) or mould (injection moulding). Equipment of both processes are also similar.

Slurry Casting Process

Slip casting method: It is a fabrication method. In this process low-viscosity slurry of ceramic powder is poured into a porous plaster mould. The porous nature of the plaster mould draws water from the slurry that contacts the mould. This process continues as the capillary section of the mould continues to draw water through the increased ceramic solids at the mould wall. After establishing a sufficiently thick wall at the mould wall, the remaining liquid is drained, dried and when the cast is sufficiently dried, the mould is removed.

There are several factors in slip casting method. The porosity of the plaster mould is controlled by water content. The particle size of the powder should be relatively coarse to permit high level of vehicle permeability through the cast wall. Slip casting is widely used commercially because it enables the casting of complex shapes from an almost unlimited variety of ceramic composition, at a low cost. The most disadvantage of this process are low production rates and relatively short life of mould.

Tape casting method: Thin sheets of flexible ceramic tape are produced by the process of tape casting. These are prepared from ceramic slurries with binder and plasticizer that are cast into thin layers on either a glass plate or an impervious polymer film and allowed to dry. It is used in electronic industries.

There are several important differences between tape and slip casting; no porous mould is used in tape casting. Vehicle used in tape casting is usually a highly volatile organic liquid, whereas standard aqueous system is used in slip casting.

Composite Fabrication Processes

The challenge in the fabrication of ceramic-matrix fibre reinforced composites is to uniformly incorporate the matrix phase around the fibres in a way that achieves full density without damaging the fibres. The most common process is slurry infiltration; this process is an extension of the polymer infiltration process used to make polymer-matrix composites. The slurry must be of sufficiently fine particle size to enable particles to penetrate the voids between the fibres.

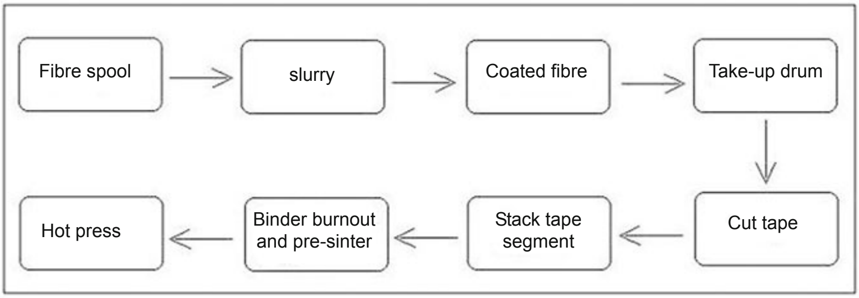

Fig. 8.9: Slurry infiltration process.

Two general processes are important in firing ceramics: vitrification and sintering. Vitrificatin occurs when constituent materials react at elevated temperatures to form a substantial amount of liquid phase, which acts to consolidate the ceramic body through the capillary forces. The sintering process has several stages that involve the following mass transport processes to varying degrees: evaporation/condensation, surface diffusion, and bulk diffusion.

Glass

8.11 INTRODUCTION

Glass, as a substance, plays an essential role in science and industry. It is an amorphous, solid material typically brittle and optically transparent. Its chemical, physical and, in particular, optical properties make it suitable for applications such as flat glass, container glass, optics and optoelectronics material, laboratory equipment, thermal insulator (glass wool), reinforcement materials (glass-reinforced plastic, glass fibre reinforced concrete), and glass art (art glass, studio glass). Silica is a common fundamental constituent of glass.

8.12 GLASS INGREDIENTS

Quartz sand (silica) is the main raw material in commercial glass production. While fused quartz (primarily composed of SiO_2) is used for some special applications, it is not very common due to its high glass transition temperature of over 1200 °C (2192 °F). Normally, other substances are added to simplify processing. One is sodium carbonate (Na_2CO_3), which lowers the glass transition temperature. However, the Na_2CO_3 makes the glass water soluble, which is usually undesirable, so lime (calcium oxide (CaO), generally obtained from limestone), some magnesium oxide (MgO) and aluminium oxide (Al_2O_3) are added to provide for a better chemical durability. The resulting glass contains about 70 to 74% silica by weight and is called a soda-lime glass. Soda-lime glasses account for about 90% of manufactured glass.

Most common glass has other ingredients added to change its properties. Lead glass or flint glass is more ‘brilliant’ because the increased refractive index causes noticeably more specular reflection and increased optical dispersion. Adding barium also increases the refractive index. Thorium oxide gives glass a high refractive index and low dispersion and was formerly used in producing high-quality lenses, but due to its radioactivity has been replaced by lanthanum oxide in modern eye glasses. Iron can be incorporated into glass to absorb infrared energy, for example in heat absorbing filters for movie projectors, while cerium(IV) oxide can be used for glass that absorbs UV wavelengths. Borosilicate glasses (e.g. pyrex) have as main constituents silica and boron oxide. They have very low coefficients of thermal expansion (7740 Pyrex COE is 32.5×10^{-7}/°C as compared to 8.36×10^{-5}/°C for one type of soda-lime glass), making them more dimensionally stable. The lower COE also makes them less subject to stress caused by thermal expansion, thus less vulnerable to cracking from thermal shock. They are commonly used for reagent bottles, optical components and household cookware. Fining agents such as sodium sulphate, sodium chloride, or antimony oxide may be added to reduce the number of air bubbles in the glass mixture. Glass batch calculation is the method by which the correct raw material mixture is determined to achieve the desired glass composition.

8.13 MANUFACTURING OF GLASS

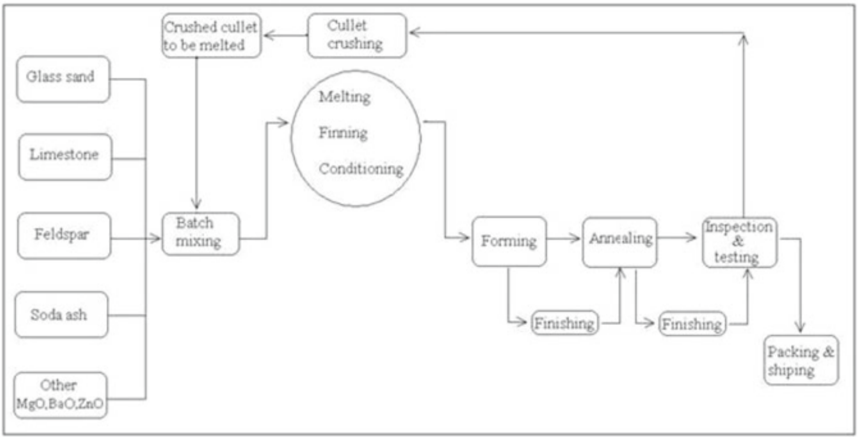

Fig. 8.10: Flow chart of glass processing.

Glass articles are manufactured by a process in which raw materials are converted at high temperatures to a homogeneous melt. Initial raw materials are selected according to purity, grain size, supply, easy melting and cost. Sand is most common ingredient. Container-glass manufacturers generally use sand between 20 and 30 mesh. Iron oxide and titanium are the primary contaminants. Limestone is the source of calcium and magnesium. It consists primarily of calcite (95%$CaCO_3$) or as a dolomitic limestone. High quality limestone contains less than 0.1% Fe_2O_3 and approximately 1% of silica and alumina. Feldspar is the common source of alumina. Boron is another raw material for manufacturing glass. Powdered anthracite coal is a common reducing agent in glass manufacture. Finning agents remove the bubbles in the molten glass and include sulphates, halides. They react by release of oxygen or sulphide trioxide.

Materials of optimum grain size are weighed carefullly, and mixed together intimately. The efficiency of the melting operation and the uniformity and quality of the glass product are very often determined in the mix house. Batch handling systems vary widely throughout the industry, from manual to fully automatic. The method by which the batch is mixed depends more on the type of glass than on the size of the tank. High SiO_2 glasses tend to be batch-mixed in pan-type mixers. The batch is first dry-blended and then small amounts of liquids are sometimes added or wet-blended. The whole operation takes 3 to 8 mins; longer treatment may unmix or segregate the batch.

Table 8.7: Examples of batch homogenization

Batch materials	*Weight kg*	*Oxides supplied, kg*							
		SiO_2	*Al_2O_3*	*FeO*	*CaO*	*MgO*	*K_2O*	*Na_2O*	*LOI*
Sand	300	299.3	0.2	0.03	-	-	-	-	0.5
Soda ash	100	100	-	-	-	-	-	58.3	41.7
Feldspar	40	26.4	7.6	0.03	0.4	-	4.1	1.3	0.1
Aragonite	90	90	-	0.02	49.0	0.2	-	-	40.7
Powdered coal	9	-	-	-	-	-	-	-	9
Iron pyrites	1.4	-	-	0.84	-	-	-	-	0.6
Cullet (crushed glass)	460	333.7	9.2	1.03	48.8	-	-	67.2	-
Salt cake	4	-	-	-	-	-	-	2.1	1.9

Table 8.7 shows by example the problem of batch homogenization, where 1 kg pyrites and 4 kg salt must be uniformly dispersed throughout a 1000 kg batch, nearly one third of which is 50 mesh sand and nearly half of which is cullet (1-2 cm) glass.

Melting

When the intimately mixed batch is charged into the hot furnace, a series of melting, dissolution, volatization and redox reactions take place between the materials in a particular order and at the appropriate temperature.

Dissolution of the more refractory grains, such as sand, is created by fluxes, e.g. sodium carbonate.

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

As the reaction continues,

$$Na_2SiO_3 + SiO_2 = Na_2Si_2O$$

Finally at about 780 °C, a mixture approaching an eutectic liquid is formed.

$3\ Na_2Si_2O_5 + SiO_2$ forms a mixture approaching.

The decomposition of alkali carbonates proceeds in a similar manner, as does their fluxing action on sand and other minerals, notably alumina-containing ones such as nepheline syenite and feldspars. Finning is the physical and chemical process of removing gas bubbles from the molten glass melt. Gas is evolved during the 1st stages of melting because of:

- decomposition of carbonates and sulphates
- air trapped between the grains of the fine grained batch materials and water evolved from the hydrated batch materials
- change in oxidation state of some of the batch materials, e.g. red lead:

$$2(Pb_3O_4) = 6PbO + O_2$$

Melting units range from small pot furnaces for manual production to large, continuous tanks for rapid machine forming. After mixing, the raw materials are charged into a furnace for melting. Pot furnaces are used for melting smaller quantities of glasses below 1400 °C. The largest furnaces are continuous regeneration furnaces that recover waste heat from burned gases. They produce large quantities of quality glass and are either cross or end-fired. Small, continuous melting tanks, filled automatically or by hand, produce high quality glass, such as optical ophthalmic glasses, at low volume. The largest furnaces are continuous regenerative furnaces that recover waste heat from burned gases. They produce large quantities of quality glass.

8.14 MECHANICAL FINISHING

Glass can be cut by the following methods:

- Sawing is done with wire or circular blades used in conjunction with loose bonded abrasive.
- In score-break glass method, the piece of glass is scored with a tool such as diamond, steel and then bent to apply tension.

- Flame cut-off is accomplished with pinpointed flames which heat the glass until it is soft enough to separate.
- Score-thermal crack-off is done by applying heat opposite a mechanically produced score on the glass surface.

Process of Mechanical Finishing

Drilling: Glass is drilled with carbide or bonded diamond drills under a suitable coolant such as water or kerosene. Other drilling processes include a metal tube rotating about its axis, an ultrasonic tool in combination with abrasive slurry, or an electron beam.

Grinding: Glass is ground with diamond, silicon carbide, garnet and sand. These materials are used loose, as in the grinding process employed for plate glass. They are bonded in grinding wheels or coated on fabric belts.

Mechanical polishing: It is more or less similar to grinding, but the polishing compound (cerium oxide, ferric oxide) is finer. The polishing tool may be plastic, cellulose and pitch. A mixture of hydrofluoric and sulphuric acids is used for acid-polishing.

8.15 CHEMICAL FINISHING

Treatment of glass surface with use of chemicals may alter its appearance and durability e.g. ion exchange helps to alter strength of glass articles. A glass, e.g., a sodium aluminosilicate, is immersed in a bath of potassium nitrate at a temperature about 50 °C below its strain point. The sodium ion is replaced by potassium ion and thus diffused from glass. Stress release is minimized because of the low process temperature. Chemical strengthening produces higher strength in thinner glass than does thermal tempering, but it is more susceptible to weakening by abrasion. Silver and copper containing mixtures can be applied to produce colours through ion exchange in glass. Sometimes acid etching or frosting with dilute hydrofluoric acid produces articles on glass surface.

Cleaning

Methods of cleaning glass are closely related with the types of glass and its uses. Cleaning requires some considerations like: the soil to be removed, the interaction between soil and glass and the effects of cleaning glass surface. Aqueous solvents are frequently used for cleaning. Organic solvents usually have no harmful effect on most glasses. Some organic solvents may be used alone or as aqueous mixtures in commercial cleansers.

8.16 GLASSMAKING IN THE LABORATORY

New chemical glass compositions techniques can be initially investigated in small-scale laboratory experiments. In the laboratory mostly pure chemicals are used. Care must be taken that the raw materials have not reacted with moisture or other chemicals in the environment (such as alkali oxides and hydroxides, alkaline earth oxides and hydroxides, or boron oxide). Evaporation losses during glass melting should be considered during the selection of the raw materials, e.g., sodium selenite may be preferred over easily evaporating SeO_2. Also, more readily reacting raw materials may be preferred over relatively inert ones, such as $Al(OH)_3$ over Al_2O_3. Usually, the melts are carried out in platinum crucibles to reduce contamination from the crucible material. Glass homogeneity is achieved by homogenizing the raw materials mixture (glass batch), by stirring the melt, and by crushing and re-melting the first melt. The obtained glass is usually annealed to prevent breakage during processing. In order to make glass from materials with poor glass forming tendencies, novel techniques are used to increase cooling rate, or reduce crystal nucleation triggers.

8.17 PROPERTIES

Thermal Properties

Thermal expansion: The thermal expansion properties, particularly the low expansions, are the primary properties that have been exploited commercially. The low expansion materials have been used for applications where thermal shock resistance is important such as cookware, stove tops, heat exchangers etc. They have also been used in applications such as mirror substrates where minimal thermally induced distortions are important. Higher expansion materials have been used for sealing various metals and alloys.

Thermal stability: The maximum use temperature must be defined in terms of a time factor and degree of loading. The crystalline phase plays an important role, but the maximum use temperature is limited by the residual glass which may crystallize further or it may enhance deformation by viscous flow. The glass ceramic materials are generally more refractory than the common glasses but less refractory than the common oxide refractories.

Optical Properties

Glass is in widespread use largely due to the production of glass compositions that are transparent to visible wavelengths of light. In contrast, polycrystalline materials do not in general transmit visible light. The individual crystallites may be transparent, but their facets (grain boundaries) reflect or scatter light resulting in diffused reflection. The surface of a glass is often smooth since during glass formation the molecules of the super cooled liquid are not forced to dispose in rigid crystal geometries and can follow surface tension, which imposes a microscopically smooth surface. These properties, which give glass its clearness, can be retained even if glass is partially light-absorbing i.e. coloured. Glass has the ability to refract, reflect and transmit light following geometrical optics, without scattering it. It is used in the manufacture of lenses and windows. Common glass has a refraction index around 1.5.

Colour

Common soda-lime float glass appears green in thick sections because of Fe^{2+} impurities. Colour in glass may be obtained by addition of electrically charged ions that are homogeneously distributed (such as in photochromic glasses). Ordinary soda-lime appears colourless to the naked eyes when it is thin, although iron (II) (FeO) impurities produce a green tint which can be viewed in thick pieces. Further FeO and additions may be used for the production of green bottles.

Soda-lime glass for containers is slightly different from soda-lime glass for windows (also called flat glass or float glass). Float glass has a higher magnesium oxide content as compared to container glass, and a lower silica and content.

Transmission

The spectral transmission of glass is determined by reflection at the glass surfaces and the optical absorption within the glass. Transmission may be controlled by the types of glass used, e.g., silicate, phosphate, borate, etc., or by the control or addition of colouring additives, melting atmosphere, melting temperatures and cooling schedules. In glasses containing suspended particles, transmissions diffuse. Oxides that are frequently used to control colour in glass are listed in Table 8.8.

Table 8.8: Colouration of glass

Effect	*Oxide*
Colourless, uv transmitting	SiO_2, P_2O_5
Colourless, uv absorbing	CeO_2, TiO_2, Fe_2O_3
Blue	CO_3O_4, S, Cu_2O+CuO
Purple	MnO_2
Brown	MnO, MnO+Fe_2O_3, NiO, TiO_2
Yellow	CdS, CeO_2+TiO_2, UO_3
Orange	CdS+Se
Green	Cr_2O_3, V_2O_3, CuO, MoO_3
Red	CdS+Se
Amber	Na_2S
Black	CO_3O_4

8.18 ECONOMIC ASPECTS

Glass manufacture is classified according to the product into flat, container, fibre, or specialty glass. The flat and container companies produce over 14×10^6 soda-lime glass per year. The specialty glass manufactured of pressed and blown ware, television bulbs, and lighting and optical glasses melt hundreds of glass compositions to fulfill the need for a large variety of products.

Various Glass Types

Flat glass: In United States, 31 flat-glass plants are operated by PPG In industries, Libbey-Owens-Ford (LOF), Food Motor Company, AFG Industries, Combustion Engineering, The West Virginia Flat Glass Company. Growth of this industry depends upon the construction and automotive markets. The float process produces 85% of all the flat glass. The remainder is thin sheet for picture glass or rolled and patterned glass. Production of the flat glass is cyclical but increases in volume by approximately 4% per year. Less than 10% of the total used is imported.

Container glass: Statistics for food, beverage, drug and cosmetic, and household and industrial containers are compiled and published by the glass packing institute (GPI). Beverage containers, including soft drink, beer, wine and liquor, constitute the largest segment followed by food, drug and cosmetic, and household. Imports are of very minute importance because of high transportation costs. Export of container glass is only about 1% of the total amount manufactured for the same reason.

Fibre glass: This glass is classified as either wool or textile. More than a dozen companies produce textile fibers for draperies, tyres, paper, etc. More than 80% of production is used for building insulation, the remainder for industrial equipment and pipe insulation. Growth of the insulation market has been faster than the textile area because of the demand for additional insulation in both new and existing building.

Specialty glass: The pressed-and-blown or hollow-ware industry is comprised of over one hundred companies in United States. The wide variety of products is divided into categories of pressed-and-blown glass for table, kitchen, art and novelty applications and products of purchased glass.

Refractory

8.19 INTRODUCTION

Refractory materials can withstand high temperature and do not fuse as these are chemically and physically stable even at a very high temperature. The oxides of aluminium, silicon, magnesium and calcium are the mostly used materials for manufacturing of refractories. Fire clays are also widely used for this purpose. Refractory materials are used in linings for furnaces, kilns and used for making other high temperature items like crucibles etc.

8.20 CLASSIFICATION OF REFRACTORY MATERIALS

Refractories are classified on the basis of (i) physical form, (ii) refractoriness (temperature stability range), (iii) chemical composition and (iv) method of manufacture.

Table 8.9: Various forms of refractories

Based on physical form	
Shaped	These have fixed size and shapes and further divided into (a) standard shapes and (b) special shapes. (a) Standard shapes have dimensions that are conformed by most refractory manufacturers and are generally applicable to kilns or furnaces of the same types. (b) Special shapes are specifically made for particular kilns or furnaces.
Unshaped	These are without definite form and are only given shape upon application. These types are better known as monolithic refractories. The common examples are ramming masses, castables, gunning masses, mortars etc.

Based on refractoriness

Type of refractory	Low heat duty refractories (LHD)	Medium heat duty refractories (MHD)	High heat duty refractories (HHD)	Super duty refractories (SD)
Refractoriness, °C	1520-1630	1630-1670	1630-1730	>1730

Based on Method of Manufacture

- Dry press process
- Fused cast
- Hand moulded
- Formed (normal, fired or chemically bonded)
- Un-formed (monolithics-plastics, gunning, castables. spraying)

Table 8.10: Types of refractories based on chemical composition

Type of refractory material	*Use*	*Description*	
Acidic refractories (e.g. silica, fire, clay etc.)	These are used in areas where slag and atmosphere are acidic. They are stable to acids but attacked by alkalis.	Aluminium-silicate refractories	These refractories vary widely in their physical, chemical and mineralogical characteristics depending on the nature and proportion of silica and alumina present on them.
		Silica refractories	These refractories consist mainly of silica. Raw materials various refractories are (97%), alkalies (<0.3%) and alumina (<10%).
Basic refractories (e.g. chromite, graphite, carbide etc.)	These are used in areas where slags and atmosphere are either acidic or basic and are chemically stable to both acids and bases.	Alumina	Manufactured from burnt bauxite, electro cast bauxite.
		Dolomite refractories	Produced by calcining natural dolomite which is mainly a mixture of lime and magnesia.
		Chrome magnesite refractories	These are mixtue of calcined magnesite and chromium oxide in various proportion necessary to develop required properties in them.
		Magnesite refractories	Produced from dead burnt magnesia (MgO).
Neutral refractories (e.g. bauxite, lime, dolomite etc.)	These are used on areas where slags and atmosphere are basic; they are stable to alkaline materials but react with acids.	Artificially used refractories	Silicon carbide, zirconium carbide etc.
		Metal used as refractories	Thorium, tungsten, iron, nickel copper etc.

Table 8.11: Firing temperature of refractories

Refractory Type	*Fireclay bricks*	*Silicon carbide bricks*	*High alumina bricks*	*Silica bricks*	*Chrome bricks*	*Direct bonded bricks*	*Magnesite bricks*
Firing temperature, °C	1250-1400	1370-1510	1450-1550	1450-1510	1450-1650	1650-1760	1450-1650

8.21 PROPERTIES OF REFRACTORY

Resistant to high temperature, heavy load, fluxes and corrosive fluids like slag are the important properties of refractories. Strength and specific gravity are some other important properties.

Refractoriness: It is the temperature at which the refractories fuse. It should be much higher than the operating temperature of the refractory.

Specific gravity: It should be low to produce more number of bricks per unit width.

Thermal conductivity: Thermal conductivity is increased when the porosity of refractory bricks decreases and the air is entrapped in refractory decreases.

Electrical conductivity: The electrical resistivity of the refractory drops rapidly with increase in temperature. For electrical furnaces, the electrical conductivity of refractory material should be low.

Strength: It is the resistance of the refractory against load shear stresses etc. In refractoriness, under load is important as some refractories fail at a lower temperature when subjected to load.

Chemical composition: Chemical composition of the refractory should be such that the surroundings do not react with refractory and corrode it.

Resistance: Erosion occurs when refractory comes in contact with metal and gas carrying dust and slag particles. Abrasion resistance of refractory is increased by using denser (low porosity), fine grained and wear resistant refractory materials.

8.22 GENERAL MODE OF MANUFACTURE

Manufacture of refractory consists of the following processes:

Grinding: It is an initial important method to ground the raw materials for obtaining proper size which is required. The ratio of coarse and fine is normally maintained at 55:45. Equipments used for this purpose are various types of crushers, hammer mills, ball mills etc.

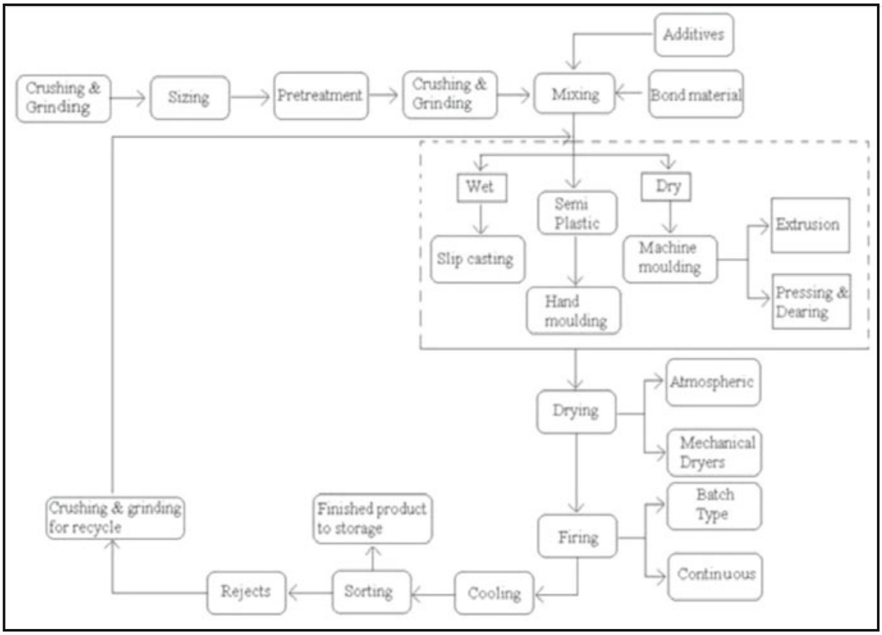

Fig. 8.11: General mode of manufacture.

Pre-Treatment: Pretreatment methods include firing at high temperature which bring about the complete mineral conversion and thus stabilize the mineral. The constituents of the finished refractory produced by reaction between the solid particles of raw materials and these refractory materials will be in equilibrium condition. Silica contains quartz which is not stable at high temperatures but undergoes transformation to its allotropic forms—tridymite and cristobalite—involving high volume changes. Tridymite, with higher symmetry, a more open structure and cristobalite with highest symmetry and the most expanded structure are two forms of polymorphs of quartz. These polymorphs are related to each other by reconstructive transformation, a process that requires considerable energy. Quartz is transformed into tridymite on very prolonged heating at 870 °C. On heating above 1470°C, this is transformed into cristobalite. Conversion of quartz into tridymite involves 16% increase in volume whereas conversion of tridymite into cristobalite involves a little contraction in volume. Similarly fireclay which consists of numerous hydrous alumina silicate minerals, breakdown to several constituents on heating and these constituent tend to form stable mullite (Al_2O_3. $2SiO_2$). Magnesite is dead burnt to eliminate all the CO_2 from it and to convert it into stable crystalline magnesia (MgO) known as 'Periclase' and involves least shrinkage in refractory materials on firing. Dolomite also is dead burnt to calcium and periclase.

Mixing: The grinded refractory materials are mixed homogeneously with the binding material (having plasticity) to facilitate easy moulding. Pugmills are used to ensure even distribution of fine and coarse particles in the whole mass. Water, additives, binding materials and mineralizers are added and the mass is mixed thoroughly to ensure homogeneity of the product (i.e. of uniform composition and uniform distribution of fine and coarse grains etc.) for easy moulding and development of useful properties of the fired refractories.

Moulding: It is done mechanically by applying high pressure or normal as suitable to increase density and strength of refractory. Moulding which follows mixing of refractory materials is done through two processes.

Hand moulding: It is carried out in wooden boxes and is cheaper than machine on a jobbing basis.

Machine moulding: Machine-moulded refractories have higher strength and density than hand-moulded refractories. Machine moulding can be used for semi-plastic mixture using moderate moulding pressures.

Drying: Drying of moulded refractories increases its green strength by removing moisture and thus making them safe for subsequent handling. It is done at slow rate to avoid voids and high shrinkage and crack formation.

Firing: Bricks are burnt into kiln to remove water of hydration, vitrification and development of stable mineral forms. Shrinkage in volume upto 3% occurs during burning. Degree of firing of silica brick is indicated by its specific gravity. High specific gravity of 2.5 indicates the presence of considerable amount of unconverted quartz in the refractory whereas a specific gravity of 2.32 to 2.37 indicates adequate firing and transformation of quartz to tridymite or cristobalite.

QUESTIONS

1. Explain how various properties of ceramics are related with their products.
2. Give a schematic diagram to focus how ceramic is made.
3. What is the relation between traditional use and modern application of ceramics.
4. Give a schematic diagram to highlight the flow chart of glass processing method.
5. Briefly describe the mechanical finishing process of glass.
6. Explain the following terms: Flat glass, Fibre glass, Specialty glass, Container glass.
7. Based on physical form, how do you classify refractory materials.
8. Give a brief description about the general mode of manufacture.

FURTHER READING

Anderson, P.W. (1995). Through the Glass Lightly. *Science*, **267(5204):** 1615. doi:10.1126/science.267.5204.1615-e.

Arora, A.K. and Tat, B.V.R. (1996). Dynamics of Charged Colloidal Suspensions Across the Freezing and Glass Transition. *In:* Ordering and Phase Transitions in Charged Colloids. VCH Publishers, New York.

Doering, Robert and Yoshio Nishi (2007). Handbook of semiconductor manufacturing technology. CRC Press.

Douglas, R.W. (1972). A history of glassmaking. G.T. Foulis & Co Ltd., Henley-on-Thames. ISBN 0-85429-117-2.

Eric Le Bourhis (2007). Glass: Mechanics and Technology. Wiley-VCH.

Greer, A. Lindsay and Mathur, N. (2005). Materials science: Changing face of the chameleon. *Nature*, **437(7063):** 1246-1247.

Klement, W., Willens, R.H. and Duwez, P.O.L. (1960). Non-crystalline Structure in Solidified Gold-Silicon Alloys. *Nature*, **187(4740):** 869. Bibcode 1960Natur.187..869K. doi:10.1038/187869b0

Leadbettera, A.J. and Wrigh, A.C. (1972). Diffraction studies of glass structure: II. The structure of vitreous germania. *Journal of Non-crystalline Solids*, **7:** 37-52. doi:10.1016/0022-3093(72)90016-6.

Liebermann, H. and Graham, C. (1976). Production of Amorphous Alloy Ribbons and Effects of Apparatus Parameters on Ribbon Dimensions. *IEEE Transactions on Magnetics*, **12(6):** 921.

Mendelev, M., Schmalian, J., Wang, C., Morris, J. and Ho, K. (2006). Interface Mobility and the Liquid-Glass Transition in a One-Component System. *Physical Review*, **B74(10)**.

Micoulaut, M. et al. (2006). Simulated structural and thermal properties of glassy and liquid germania. *Physical Review*, **E73(3):** 031504. doi:10.1103/PhysRevE.73.031504. http://link.aps.org/doi/10.1103/PhysRevE.73.031504.

Ojovan, M.I. (2004). Glass Formation in Amorphous SiO_2 as a Percolation Phase Transition in a System of Network Defects. *JETP Letters*, **79(12):** 632-634.

Ojovan, M.I. and Lee, W.E. (2006). Topologically disordered systems at the glass transition. *J. Phys.: Condensed Matter*, **18(50):** 11507-11520. Bibcode 2006JPCM...1811507O. doi:10.1088/0953-8984/18/50/007.

Pfaender, Heinz G. (1996). Schott guide to glass. Springer. ISBN 978-0-412-62060-7. http://books.google.com/books?id=v5q4Hje3iFgC&pg=PA135. Retrieved 8 February 2011.

Ponnambalam, V., Joseph Poon, S. and Shiflet, Gary J. (2004). Fe-based bulk metallic glasses with diameter thickness larger than one centimeter. *Journal of Materials Research*, **19(5):** 1320. Bibcode 2004JMatR..19.1320P. doi:10.1557/JMR.2004.0176.

Pusey, P.N., Van Megen, W. (1987). Observation of a glass transition in suspensions of spherical colloidal particles. *Physical Review Letters*, **59(18):** 2083-2086. Bibcode 1987PhRvL.59.2083P. doi:10.1103/PhysRevLett.59.2083. PMID 10035413.

Salmon, P.S. et al. (2006). Glass Fragility and Atomic Ordering on the Intermediate and Extended Range. *Physical Review Letters*, **96(23):** 235502. Bibcode 1976ITM...12.921L. doi:10.1109/TMAG.1976.1059201.

Shackelford, James F. and Doremus, Robert H. (2008). Ceramic and Glass Materials: Structure, Properties and Processing. Springer. ISBN 0-387-73361-2.

Van Megen, W. and Underwood, S. (1993). Dynamic-light-scattering study of glasses of hard colloidal spheres. *Physical Review*, **E47:** 248. Bibcode 1993PhRvE.47.248V. doi:10.1103/PhysRevE.47.248.

Werner, Vogel (1994). Glass Chemistry (2 ed.). Springer-Verlag, Berlin and Heidelberg GmbH & Co. K. ISBN 3-540-57572-3.

Zallen, R. (1983). The Physics of Amorphous Solids. John Wiley, New York. ISBN 0-471-01968-2Löwen, H.

Zanotto, Edgar Dutra (1998). Do Cathedral Glasses Flow? *American Journal of Physics*, **66(5):** 392-396. Bibcode 1998AmJPh.66.392Z. doi:10.1119/1.19026.

CHAPTER

9

CLAYS FOR MEDICINES AND FILLERS

9.1 ROLE OF CLAY IN MEDICAL SCIENCE

Clay plays an important role in medical science to prepare various medicines. This special aspect of clay is known as clay therapy. It is based on the ability of clays and clay minerals to adsorb and retain harmful and toxic substances. The beneficial effects of these materials to human health, notably in the treatment of gastrointestinal disorders, have been recognized. Among the variety of clays and clay minerals that were used by primitive tribes are bentonite, kaolinite, montmorillonite and smectite. The word medicine is derived from the Latin word "*medicina*". Medicine is the science and art of healing. It encompasses a variety of health care practices evolved to maintain and restore health by the prevention and treatment of illness in human beings. Prehistoric medicine incorporated plants, animal parts and minerals.

9.2 ADSORPTIVE PROPERTIES OF CLAY MINERALS

A. Microorganisms

In the stomach, *Helicobacter pylori* is associated with gastritis and gastroduodenal ulcers. This bacterium is also one of the most important ethiopathogenic factors causing peptic ulcer. Smectite, on HeLa cells infected by *H. pylori* isolated from human biopsies, significantly reduces adhesion of the bacteria to the surface of epithelial cells. This is why smectite is effective in treating the symptoms of people with non-ulcer dyspepsia who are infected by *H. pylori*. Clay minerals are efficient drugs for treating disorders of the gastrointestinal mucosa, induced by microorganisms. Kaolinite and montmorillonite are capable of adsorbing viruses. As such, these minerals can induce rapid recovery when administered to children suffering from

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gastroenteritis. Similarly, the strong adsorptive power of smectite lies behind its ability to aggregate bacteria. In the intestine, smectite is effective against diarrhoea as shown by clinical data for new-born calves with neonatal gastroenteritis.

B. Gas

Clay minerals can serve as gas adsorbents in patients with symptoms of flatulence and abdominal distension. Thus, smectite can reduce the amount of hydrogen emitted during colonic fermentation.

C. Alimentary Allergy

Food allergy is also responsible for disturbances in colonic transit, water absorption and intestinal permeability. Guinea pigs that were sensitized by b-lactoglobulin from cow milk show colonic transit acceleration, a colonic hypersecretory response, a strong increase in intestinal permeability, and a decrease in faecal dry matter. These effects are not observed in animals that were treated with smectite. Clays can inhibit anaphylaxia probably by controlling the release of mediators at the origin of the degranulation of the mast cells.

D. Toxins

Due to adsorptive property, clays can adsorb a variety of toxic substances, such as strychnine, mycotoxins, aflatoxin and toxins. Clay can provide active protection against disturbances during gastrointestinal transit. However, if the toxin is incubated with smectite for 24 h beforehand, no increase in the rate of gastric emptying and small intestinal transit occurs. Smectite can also adsorb the enterotoxin of *Clostridium difficile*. In rats, this toxin causes intestinal permeability to increase through hypersecretion of colonic water.

E. Pesticides

Clay minerals can also protect the digestive mucosa against pesticide damage. Diquat, a widely used non-selective desiccant herbicide, induces erosion of intestinal mucosa and fluid hypersecretion. Similarly, montmorillonite and bentonite are good adsorbents, and may be recommended for the treatment of pesticide poisoning.

9.3 USEFULNESS OF CLAY IN CLINICAL ASPECT

Clay minerals are efficient against several ‘aggressors’ that cause major disorders of the gut. These beneficial effects of clay minerals are associated with their toxic secretions and modification of the thickness and rheological properties of the adherent mucus.

Clay minerals are efficacious against several aggressive agents causing severe intestinal disorders due to good adsorbents properties. By adsorbing viruses, bacteria clay minerals can reduce the occurrence of prolonged diarrhea. Simultaneously these minerals do not interfere with the electrolyte balance and so, are easily tolerated by patients. Clay minerals also provide protection against diarrhoea induced by antibiotic treatments. Clay minerals are promising drugs in the treatment of irritable bowel syndrome (IBS), a rather frequent disease in adults with a complex pathogenic mechanism.

9.4 INTERACTIONS OF CLAY MINERALS WITH GASTROINTESTINAL MUCUS

The mucus gel is largely composed of glycoprotein polymers, lipids and proteins, linked together by covalent bonds. As such, it acts as a physical barrier protecting the mucosa against penetration by extraneous molecules and mechanical injury. By maintaining a pH gradient and competing with the epithelial surface for microorganisms, the mucus gel also acts as a chemical barrier. Thus, a weakening of the mucus gel barrier may be at the origin of disorders. The short-term treatment with clay minerals, such as smectites, increases the thickness of the adherent mucus. These may be ascribed to interactions of mineral particles with mucus components, by which the gastrointestinal glycoproteins are modified and their polymerization is enhanced. Similarly bohemite reduce mucus degradation. The beneficial effects of minerals are also associated with improvements in the rheological properties of the mucus gel. This reflects the increased extent of polymerization, and the improvement in quality, of the adherent mucus. Clay minerals help to bring changes in physico-chemical properties.

9.5 MEDICAL CARE

The provision of medical care is classified as primary care, secondary care and tertiary care as shown in Table 9.1.

Table 9.1: Provision of medical care

Primary care	This kind of services is provided by physicians and/or medical assistants.
Secondary care	Patients needing more medical care are referred/treated in medical centres.
Tertiary care	Patients needing specialized medical treatment are provided by specialist medical centre.

In all these stages of treatment, tablet medicines used contain clay filler as medium factor. Variation of strength of medicine is controlled by amount of filler used during tablet preparation.

9.6 CLAY MINERALS IN PHARMACEUTICAL FORMULATIONS

The use of clay minerals in pharmaceutical formulations was described by many authors (Del Pozo 1978, 1979; Gala´n et al., 1985; Bech, 1987; Cornejo, Kaolinite, talc, palygorskite and smectites are used for therapeutic purposes in pharmaceutical formulations as active principles or excipients. The possible use of sepiolite as active principle or excipient in pharmaceutical formulations was also investigated and there are commercial medicines that include sepiolite in its composition (as active principle and excipient). The fundamental properties for which clay minerals are used in pharmaceutical formulations are high specific area and having sorptive capacity and favourable rheological characteristics.

9.7 MAIN PROPERTIES OF CLAY MINERALS USEFUL IN AESTHETIC MEDICINES

1. Appropriate rheological properties for the formation of a viscous and consistent paste; and good properties for easy application, and adherence to the skin during treatment.
2. High heat-retention capacity: As heat is also a therapeutic agent, clay minerals are applied hot to treat chronic rheumatic inflammations, spot traumatisms and dermatological problems.
3. High sorption capacity: Clays can eliminate excess grease and toxins from skin, and hence are very effective against dermatological diseases such as boils, acne, ulcers, abscess and seborrhoea. An organic active principle can also be incorporated into the clay mineral before its application to the patient's skin for therapeutic purposes.
4. Softness and small particle size since the application of the mud, particularly as face mask, can otherwise be unpleasant.
5. Smectites (bentonite clays) fulfil many of the requirements for usage in spa and beauty therapy.

9.8 IMPORTANCE OF FILLERS

The term 'Filler' indicates something used to fill gaps; mainly fillers are particles added to material (plastics, composite material and concrete) to improve some properties of the mixture material. Worldwide more than 53 million tons of fillers are used every year in different application areas, such as paper, plastics, rubber, paints, coatings, adhesives and sealants. As such, fillers, produced by huge number of companies, rank among the world's major raw materials and are a major constituent in a variety of goods for daily consumer needs.

9.9 TYPES OF FILLER

Formerly, fillers were used predominantly for final finishing of end products, in which case they are called extenders. Among the 21 most important fillers, calcium carbonate holds the largest market volume and is mainly used in the plastics sector.

In some cases, fillers also enhance properties of the products, e.g. in composites. In such cases, a beneficial chemical interaction develops between the host material and the filler. As a result, a number of optimized types of fillers or surface treated goods have been developed.

Table 9.2: Uses of clay minerals as fillers

Industry	*Clay family*
Plastics, rubber, paper industry	Kaolin, talcum, pyrophyllite
Cosmetics, plastics	Palygorskite, sepiolite

9.10 CLAY AS FILLER

Composition

This discussion will be limited to kaolin, the most common form of clay added to paper as a filler. Bentonite is a generic term for montmorillonite clay. Kaolin is a hydrated silica-aluminate. Deposits of kaolin particles have been built up by natural geologic processes. In one of these processes the kaolinite is initially released by glaciation. Rivers carry silt in the glacial runoff and deposit it in shallow seas. Larger particles settle first, then the finer ones, usually at a different location. By choosing their locations, clay producers have access to a range of particle sizes and brightness of kaolin particles. High quality deposits of kaolin, having moderately high brightness and uniform particle size are found all over the world, especially in China, Georgia, Brazil and England. Anionic dispersants such as phosphates and acrylates are usually added to clay as it is collected and processed. The particles are typically irregular hexagons with a layered underlying structure. The size is highly variable; filler clays usually are selected with an average (SEM) particle size of about 1 to 3 micrometres. When the kaolin is first released it is likely to contain dark and abrasive impurities. Processing steps can include sieving, centrifugal cleaning, magnetic removal of dark contaminants, and bleaching. After these processes the particles of kaolin is still likely to resemble “books,” comprised of layers. This is the most common type of clay used for paper filling, especially when it is important to maintain strength at a given filler level. Extended agitation of clay slurries in the presence of hard ceramic balls (of visible size, much larger than the kaolin particles) causes the kaolin to delaminate into thinner platelets. This is delaminated clay.

Function

Besides reducing the cost of paper, clays are especially useful for creation of gloss (in highly filled, supercalendered papers), for increasing resistance to air flow (in the case of delaminated clays), and for imparting a moderate decrease in the friction coefficient of paper (especially when added to the size-press solution).

Strategies for Use

The main concerns are (a) How high a filler level is best?; and (b) How to achieve an adequate retention?

A uniform dispersion of clay can be obtained with conventional dispersing equipment, e.g. a Cowles mill. Also it is possible to get bulk delivery of clay slurries with solid levels in the neighbourhood of 70%. The price that one pays for the convenience of using pre-slurried clay is that it contains anionic dispersants. These can make retention more difficult. Coating grades of clay are especially difficult to handle at high levels in the wet end due to the combination of dispersants, higher surface area, and smaller particles that are harder to filter from the water as the paper is being formed. The content of clay in paper usually is limited by decreasing strength properties and decreasing caliper at a given smoothness and basic weight. Clay tends to produce dense paper, especially when it is calendered. Unlike calcium carbonate fillers, clay products can be used at any pH. Clay will form agglomerates if prematurely mixed with such additives as cationic starch, alum, retention aids and the like. Intentional agglomeration of filler is a potential way to increase the strength of paper at a given filler content; however this technology has not become widely used. Most retention aid systems are effective with clay. Ashing of the paper at 900 °C drives off waters of hydration. If a paper sheet is assumed to contain only hydrous kaolin (not calcined clay), the percent ash needs to be divided by 0.86 to estimate the percent of clay originally present in the paper.

Cautions

Normal precautions regarding dust need to be observed when clay is received as a dry powder.

9.11 USES OF FILLER

Fillers are used for packaging, mainly for food. These are used to fill either a bottle or a pouch, depending on the product. There are several types of fillers used by the packaging industry, those listed below are the most common.

- **Auger/Agitator Filling Machine:** This machine is designed as to fill dry mixes, such as flour and sugar. The fillers have a hopper shape like a cone that holds the mix and puts it in a pouch using an auger screw that is controlled by the agitator and so it's called Agitator Filling Machine.

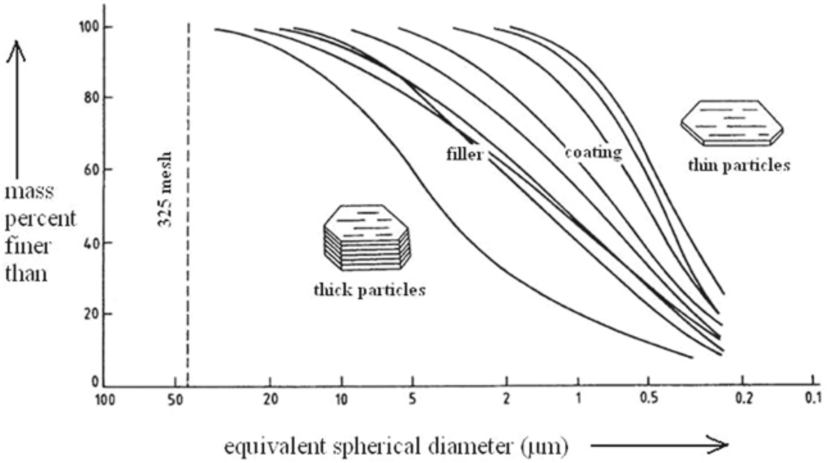


Fig. 9.1: Kaoline particle size, particle size distributions of clay products commonly used for paper filling and coating.
Source: Hagemeyer (1984), Pigments for Paper.

- **Fillers act in medical purpose:** These are designed for products that are counted by pieces instead of weight. These are designed for 256 small bottles, but the hopper of the filler is set up to permit scan counting of tablets or candy pieces.
- **Positive Displacement Pump Fillers:** Positive displacement pump filling machines easily handle a wide range of container sizes, fill volumes and product types. While originally designed for filling creams, gels and lotions, these fillers also handle water thin and heavy paste products.

QUESTIONS

1. Using adsorptive properties, explain the application of clay minerals in medicine.
2. How do microorganisms help in producing medicines.
3. In aesthetic medicines, what is the usefulness of clay minerals.
4. What is the relation between clay families and industries.
5. Describe the uses of fillers.

FURTHER READING

Abdel-Halim, Rabie E. (2006). Contributions of Muhadhdhab Al-Deen Al-Baghdadi to the progress of medicine and urology. *Saudi Medical Journal*, **27(11):** 1631-1641.

Addison, K., Braden, J.H., Cupp, J.E., Emmert, D. et al. (2005). (AHIMA e-HIM Work Group on the Legal Health Record) Update: Guidelines for Defining the Legal

Health Record for Disclosure Purposes. *Journal of AHIMA*, **78(8):** 64A-G. PMID 16245584.

Chairman's Reflections (2004). Traditional Medicine Among Gulf Arabs, Part II: Blood-letting. *Heart Views*, **5(2):** 74-85.

Coulehan, J.L. and Block, M.R. (2005). The Medical Interview: Mastering Skills for Clinical Practice (5th ed.). F.A. Davis. ISBN 0-8036-1246-X. OCLC 232304023.

Ezzo, J., Bausell, B., Moerman, D.E., Berman, B. and Hadhazy, V. (2001). Reviewing the reviews. How strong is the evidence? How clear are the conclusions? *Int J Technol Assess Health Care*, **17(4):** 457-466. PMID 11758290.

Farmer, Paul (2001). The major infectious diseases in the world—To treat or not to treat? *The New England Journal of Medicine*.

Grammaticos, P.C. and Diamantis, A. (2008). Useful known and unknown views of the father of modern medicine, Hippocrates and his teacher Democritus. *Hellenic Journal of Nuclear Medicine*, **11(1):** 2-4. PMID 18392218.

Grove, W.H., Zald, D.H., Lebow, B.S., Snitz, B.E. and Nelson, C. (2000). Clinical versus mechanical prediction: A meta-analysis. *Psychological Assessment*, **12(1):** 19-30. doi:10.1037/1040-3590.12.1.19.

Harvey, C.C. and Murray, H.H. (1993). The geology, mineralogy and exploitation of halloysite clays of Northland, New Zealand. *In:* Murray, H.H., Bundy, W.M. and Harvey, C.C. (eds), Kaolin Genesis and Utilization. The Clay Minerals Society.

Longfellow, H.W. (2002). History of Plastic Surgery in India. *Journal of Postgraduate Medicine*.

Madigan, M. and Martinko, J. (2006). Brock Biology of Microorganisms (11th ed.). Prentice Hall. ISBN 0-13-144329-1.

Martín-Araguz, A., Bustamante-Martínez, C., Fernández-Armayor Ajo, V. and Moreno-Martínez, J.M. (2002). Neuroscience in al-Andalus and its influence on medieval scholastic medicine. *Revista de neurología*, **34(9):** 877-892. PMID 12134355.

Murray, H.H. (1999). Applied clay mineralogy today and tomorrow. *Clay Minerals*, **34:** 39-49.

Murray, H.H. (2000). Traditional and new applications for kaolin, smectite, and palygorskite: A general overview. *Applied Clay Science*, **17:** 207-221.

Singh, A. and Sarangi, D. (2003). We need to think and act. *Indian Journal of Plastic Surgery*.

Zimmer, Carl (2004). Soul Made Flesh: The Discovery of the Brain – and How It Changed the World. Free Press, New York.

CHAPTER

10

SOIL CONDITIONER AND FERTILIZER INDUSTRY

10.1 NECESSITY OF SOIL CONDITIONER

A soil conditioner is a material added to soil to improve its overall condition, especially plant growth and health and simultaneously it corrects the soil's deficiencies in structure and/or nutrients. It is also called a soil amendment. Physical conditions of soil such as porosity and permeability will be improved by using the materials for agriculture purpose, known as fertilizer. Here the type of conditioner depends on current soil composition and the type of plant. Some soils lack nutrients necessary for proper plant growth. Some examples of soil conditioner include peat, coffee grounds, compost tea, fertilizers, lime, and vermiculite and sphagnum moss. Beside this, mechanical property of soil also needs to be improved for some engineering aspects such as construction of dam, bridge etc. Thus the soil conditioner plays an important role to increase strength of soil.

10.2 ACTIVITIES OF SOIL CONDITIONER

Poor physical condition of soil can restrict water intake into the soil and subsequent movement, plant root development, and aeration of the soil. Producers and researchers alike are interested in improving the physical condition of the soil and, thus, enhance crop production. These goals can be accomplished in part through the use of good management techniques. In addition, there are amending materials that claim to improve the soil physical condition. Soil conditioners vary greatly in their composition, application rate, and expected or claimed mode of action. Claims for various products include, but are not limited to:

S. Mukherjee, *The Science of Clays: Applications in Industry, Engineering and Environment*,
DOI 10.1007/978-94-007-6683-9_10,

- Increased water-holding capacity
- Reduced compaction and hardpan conditions
- Improved soil structure and aeration
- Alkali soil reclamation
- Increased availability of water to plants
- Better root development
- Improved tile drainage effectiveness
- Better chemical incorporation
- Higher yields and quality
- Release of “locked” nutrients

It is important to understand the nature, use and practical benefits of these products. Water-holding capacity, availability of water to plants, and drainage effectiveness are the three properties depending on porosity of soil. Porosity is influenced by presence of soil conditioner.

10.3 TYPES OF SOIL CONDITIONERS

Soil conditioners vary in both their origin and composition. Soil conditioners can be synthetic or naturally occurring; organic or inorganic.

Organic Soil Conditioners

Organic soil matter is defined as the organic fraction of the soil and includes plant and animal residues at various stages of decomposition, cells and tissues of organisms, and compounds synthesized by the soil organism population. Soil organic matter contains a wide array of compounds ranging from fats, carbohydrates and proteins to high molecular weight humic and fulvic acids. Both the diversity of compounds and the interaction of the different compounds are important in the beneficial effect attributed to organic matter. Soil organic matter is usually less than 10 per cent of the total weight of mineral soils. The beneficial effects of organic matter (humus) in the improvement or maintenance of soil physical properties has long been known. Soil organic matter serves as a reservoir for nutrients; improves soil structure, drainage, aeration, cation exchange capacity, buffering capacity, and water-holding capacity; and provides a source of food for microorganisms. Generally speaking, soils higher in organic matter have improved soil physical conditions as compared to similar soils lower in organic matter. For these reasons, many marketed soil conditioners try to emulate organic matter for improving soil physical properties.

The ratio of carbon to nitrogen (C:N ratio) of organic matter in surface soils commonly ranges between 8:1 and 15:1, with the median C:N ratio between 10:1 and 12:1. The C:N ratio of organic materials (Table 10.1) added to the soil is important in the availability of nitrogen and the rate of decay of the organic material. Competition for available nitrogen in the soil occurs when organic materials with wide or large C:N ratios are added to soil.

Table 10.1: Carbon:nitrogen ratios of organic material and soil microbes

	Material	*C:N ratio*
Crop residues	Clovers (mature)	20:1
	Alfalfa (young)	13:1
	Bluegrass	30:1
	Straw (small grain)	80:1
	Corn stalks	40:1
	Cattle manure	30:1
	Peat moss	58:1
	Sewage sludge	10-12:1
Soil microbes	Bacteria	5:1
	Fungi	10:1
	Actinomycetes	6:1
Sawdust	Pine	729:1
	Hardwood	295:1

Mineral Conditioners

Gypsum has long been recognized for its benefits on high sodium-containing soils. Gypsum is a mineral with the chemical composition $CaSO_4.2H_2O$. It occurs in nature as soft crystalline rock and varies in purity. Gypsum has been shown to displace exchangeable sodium from the cation exchange sites of soils high in sodium. With irrigation or dryland, gypsum can be used to reclaim saline areas or slick spots, soften and crumble alkali hard pans, supply calcium on low exchange capacity soils, and improve infiltration for some puddled soils. Gypsum is not recommended on soils containing native gypsum or areas irrigated with water containing abundant amounts of calcium and magnesium. The amount of gypsum to apply depends on the purity of the gypsum and the quantity of sodium present in the soil. Actual rates should be based on a salt-alkali soil test.

Table 10.2: Materials used as conditioners

Materials	*Use*
Lime	Used to make soil less acidic
Gypsum	Used to release nutrients and improve soil structure
Peat, clay, vermiculite	Helps to make soil hold more water
Fertilizers	Digestate or compost adds depleted plant nutrients
Mulches	Used to help the soil retain moisture and nutrients so that plants remain healthy

Many soil conditioners are designed to improve soil structure in some way. Soils tend to become compacted over time, which is bad for plants, and soil conditioners can add more loft and texture to keep the soil loose. They also add nutrients, enriching the soil and allowing plants to grow bigger and stronger. Soil conditioners may be used to improve water retention in dry, coarse soils which are not holding water well, and they can be added to adjust the pH of the soil to meet the needs of specific plants or to make highly acidic or alkaline soils more usable. Before applying soil conditioner, it is a good idea to perform soil testing to learn more about the composition and structure of the soil, as this testing will determine which conditioners will be more appropriate for the conditions.

Advantage of conditioners: Soil conditioners are added to improve the soil quality. It can be used to rebuild soils which have been damaged by improper management, to make poor soils more usable, and to maintain soils in peak condition. A wide variety of products can be used to manage soil quality.

Disadvantage of conditioners: Soil conditioners are not productive when they are added in excess; over fertilization can make some plants sick, and it also generates runoff into neighbouring waterways, which is harmful for the environment.

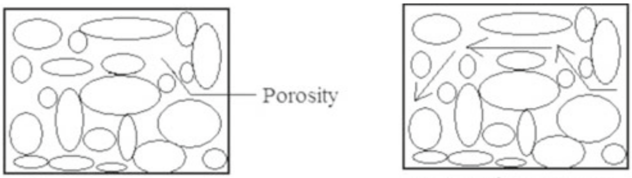
Examples: Compost can be produced at home, along with compost tea. Coffee grounds can often be obtained for free from restaurants and coffee houses. Some examples of soil conditioner include: bonemeal, peat, coir, manure, straw, vermiculite, sulfur, lime, blood meal, chemical fertilizers and sphagnum moss. Mulches are also a form of soil conditioner, as they are used to help the soil retain moisture and nutrients so that plants remain healthy.

10.4 MEASURING PHYSICAL PROPERTIES OF SOIL

A variety of soil physical measurements can be used to evaluate the effectiveness of soil conditioners. These measurements include infiltration rate, air permeability, porosity, aggregate stability, penetration resistance, or bulk density. Reliable standardized procedures are needed to compare and/or evaluate the effect of soil conditioners on soil physical properties. For example, many companies rely on penetrometer measurements to evaluate their product, but do not standardize their measurements with respect to moisture content or bulk density. Such non-standardized observations may easily lead to erroneous claims about the product. Also, be cautious of studies relying on measurements that are not easily quantified such as soil tilth, stickiness, tightness, or hardness.

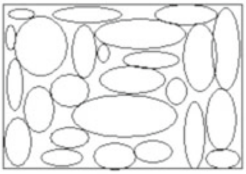
Table 10.3: Some physical properties of soil

Physical properties	*Description*	*Controlling process*
Porosity	Porosity is a measure of the fraction of the volume of voids over the total volume in a material.	With presence of soil conditioner void space of a material can be altered.
Permeability	A measure of the ability of a material to transmit fluids.	Permeability depends on the porosity and so changing of porosity also alters the permeability.
Bulk density	It is defined as the mass of many particles of the material divided by the total volume they occupy.	With increase of porosity and permeability bulk density will be decreased. Soil conditioner plays an important role to increase the bulk density.
Infiltration rate	Infiltration rate in soil science is a measure of the rate at which soil is able to absorb rainfall or irrigation.	Infiltration is the process by which water on the ground surface enters the soil. Connected void spaces are primary factor which is controlled by presence of porosity.
Aggregate stability	Aggregate stability refers to the ability of soil aggregates to resist disruption when outside forces are applied.	Aggregation affect erosion and movement of water. Desirable aggregates are stable against rainfall and water movement. Pore space between aggregates are essential for water and air entry and exchange. These pore space provides zones of weakness through which plant root can grow. Aggregation is less important where rock has low bulk density with large pore space.



Void spaces between two grains are porosity

Connected pore spaces indicates permeability with arrow sign.



Bulk density is high due to low porosity

Fig. 10.1: Diagrammatical representation of physical properties of soil.

10.5 CHANGING PHYSICAL PROPERTIES OF SOIL

A wide variety of conditioners, which claim to improve a number of soil physical properties, are commercially available today. Some of the claimed benefits include improved water holding capacity, infiltration, drainage, soil structure, aeration, aggregate stability, organic matter content, and certain chemical properties. The interrelating nature of these soil properties makes it difficult to single out the exact effect of a specific soil conditioner. All conditioner promotions, however, imply improved plant growth in response to their soil conditioning effect. Soil conditioners will not behave in the same manner and with the same results on all soil types. Different soil types vary greatly in physical, chemical and biological properties, which influence the effectiveness of soil conditioners. For instance, gypsum may improve infiltration on high-sodium soils but may be of no benefit on non-sodic soils or soils already high in gypsum. The addition of large amounts of organic material will be more effective on soils with very low organic matter levels than on higher organic matter soils. It is very important to know the soil properties under which the product was evaluated. Recommended application rates of soil conditioners range from less than a pound/acre for some synthetic or biological soil conditioners to several tons/acre for gypsum or manure. For soil conditioners that attempt to emulate soil organic matter, the application rate should be evaluated in comparison to the amount of organic matter already present in the soil.

10.6 FERTILIZER

Fertilizer is any organic or inorganic material of natural or synthetic origin that is added to a soil to increase fertility of soil as it supplies one or more plant nutrients essential to the growth of plants. Fertilizers provide six macronutrients and seven micronutrients in varying proportions:

Six macronutrients: Nitrogen (N), potassium (K), phosphorous (P), sulphur (S), magnesium (Mg), calcium (Ca)

Seven micronutrients: Chloride (Cl), boron (B), manganese (Mn), iron (Fe), copper (Cu), molybdenum (Mo), zinc (Zn)

Only three other macronutrients are required by all plants: carbon, hydrogen and oxygen. The macronutrients are consumed in large quantities and present in plant tissues and micronutrients are consumed in small quantities and also present in plant tissues.

Fertilizers come in various forms. The most typical form is granular fertilizer and the next most common form is liquid fertilizer. Some advantages of liquid fertilizer are its immediate effect. There are also slow-release fertilizers which reduce the problem of “burning” the plants due to excess nitrogen.

10.7 SEVERAL FUNCTIONS OF FERTILIZERS

1. It provides direct food for plants to promote plant growth.
2. It provides special food for specific plant and replenishes soil depletion.
3. It helps transform material and soil substance into more soluble form for the plant food.
4. It serves to neutralize unhealthy acidity or alkalinity of soil.
5. It gives strength to plant bodies to make them more vigorous and resistant to diseases.

The common fertilizer materials are given as:

1. Potash minerals
2. Nitrogen and nitrate bearing minerals
3. Phosphate minerals
4. Sulphur bearing minerals

Table 10.4: Various fertilizers with examples

Types of fertilizers	*Description*	*Example*
Potash minerals	The potash deposits have some modes of occurrences which are as marine evaporates, placer deposits etc. K is a constant of such common minerals such as orthoclase feldspar, muscovite, mica etc. While micas are resistant to weathering, orthoclase feldspar becomes decomposed very easily and its potassium content is then carried away in solution by running water and deposited along with bed in sea. Due to evaporation of sea water, large amount of K salts remain as residual product.	Orthoclase feldspar
Nitrogen and nitrate minerals	The natural occurrences may be deposits of Na nitrate ($NaNO_3$) with minor amount of potassium nitrate (KNO_3). Ammonium sulphate, another source of nitrogen, is produced during the preparation of coal gas from coal. The nitrogen-rich fertilizer ammonium nitrate is also used as an oxidizing agent in improvised explosive devices, sometimes called fertilizer bombs, leading to sales regulations.	Potash Nitrate
Phosphate minerals	Phosphate is important for plants. It plays a vital role in photosynthesis, i.e. growth. So phosphates form an important group of fertilizers and usually are prepared from apatite by treatment with H_2SO_4. The sources of phosphate minerals may be marine sedimentary phosphate bed, phosphetic	Apatite

(*Contd.*)

Table 10.4 (*Contd.*)

Types of fertilizers	*Description*	*Example*
	modules and apaptite deposits. The most important occurrence are marine beds. Singhbhum nodules and trichinopally nodules form important occurrences.	
Sulphur bearing minerals	Raw sulphur dust and sulphuric acid are added to soil to neutralize alkalinity and to reduce S deficiency since sulphur is an important food for plant. S in the soil prevents the absorption of selenium by plants. Sulphur is chiefly used as sulphuric acid to form superphosphate by the action of phosphatic mineral with H_2SO_4.	Gypsum

10.8 FERTILIZATION OF SOILS

The use of manure for fertilizing the soil is probably as old as agriculture itself. The Romans had even a particular God, Sterculius, to preside over the protection of fertility of the soil. The use of commercial fertilizers is relatively of recent origin. Fertilizer consumption in India is 69 kg of plant nutrient per hectare of arable land. The common fertilizers and the nutrients they provide are shown in Table 10.5.

Table 10.5: Name of nutrients and their corresponding percentage

Name of nutrients	*Percentage of nutrients*
Sulphate of ammonia	20.5% N
Urea	45% N
Potassium chloride	39-42% K
Ammonium nitrate	35% N
Rock phosphate	11-15% P
Bone meal	7-13% P
Super phosphate	7-8% P
Basic slag	2-8% P

10.9 TYPES OF FERTILIZERS

Fertilizers are broadly divided into organic fertilizers and inorganic fertilizers.

Organic fertilizers: Composed of enriched organic matter—plant or animal.

Inorganic fertilizers: Composed of synthetic chemicals and/or minerals.

Inorganic Fertilizer (Synthetic Fertilizer)

Inorganic fertilizer is often synthesized using the Haber-Bosch process, which produces ammonia as the end product. This ammonia is used as a feedstock for other nitrogen fertilizers, such as anhydrous ammonium nitrate and urea. These concentrated products may be diluted with water to form a concentrated liquid fertilizer. Ammonia can be combined with rock phosphate and potassium fertilizer in the Odda Process to produce compound fertilizer.

10.10 DISADVANTAGES OF INORGANIC FERTILIZER

(a) Trace mineral depletion

Many inorganic fertilizers may not replace trace mineral elements in the soil which become gradually depleted by crops. Studies have linked this depletion with marked fall (up to 75%) in the quantities of such minerals present in fruits and vegetables.

(b) Over-fertilization

Over-fertilization of a vital nutrient can be as detrimental as under-fertilization. 'Fertilizer burn' can occur when too much fertilizer is applied, resulting in a drying out of the roots and damage or even death of the plant.

(c) High energy consumption

A 2002 report suggested that the production of ammonia consumes about 5% of global natural gas consumption, which is somewhat under 2% of world energy production. Ammonia is overwhelmingly produced from natural gas, but other energy sources, together with a hydrogen source, can be used for the production of nitrogen compounds suitable for fertilizers. The cost of natural gas makes up about 90% of the cost of producing ammonia. The increase in price of natural gases over the past decade, along with other factors such as increasing demand, have contributed to an increase in fertilizer price.

(d) Long-term sustainability

Inorganic fertilizers are now produced in ways which theoretically cannot be continued indefinitely by definition as the resources used in their production are non-renewable. Potassium and phosphorus come from mines and such resources are limited. However, more effective fertilizer utilization practices may decrease present usage from mines. Improved knowledge of crop production practices can potentially decrease fertilizer usage of P and K without reducing the critical need to improve and increase crop yields. Artificial nitrogen fertilizers are typically synthesized using fossil fuels such as natural gas and coal, which are limited resources.

10.11 ORGANIC FERTILIZER

Organic fertilizers include naturally occurring organic materials (e.g. worm castings, seaweed), or naturally occurring mineral deposits.

(a) Benefits of organic fertilizer

Organic fertilizers have been known to improve biodiversity (soil life) and long-term productivity of soil, and may prove a large depository for excess carbon dioxide.

Organic nutrients increase the abundance of soil organisms by providing organic matter and micronutrients for organisms and can drastically reduce external inputs of pesticides, energy and fertilizer, at the cost of decreased yield.

(b) Disadvantages of organic fertilizers

- Organic fertilizers may contain pathogens and other disease causing organisms if not properly composted.
- Nutrient contents are very variable and their release to available forms that the plant can use may not occur at the right plant growth stage.
- More expensive to produce.

(c) Example of organic fertilizer

- Chicken litter, which consists of chicken manure mixed with sawdust, is an organic fertilizer. Researchers at the Agricultural Research Service (ARS) studied the effects of using chicken litter, an organic fertilizer, versus synthetic fertilizers on cotton fields, and found that fields fertilized with chicken litter had a 12% increase in cotton yields over fields fertilized with synthetic fertilizer.
- Other ARS studies have found that algae used to capture nitrogen and phosphorus runoff from agricultural fields cannot only prevent water contamination of these nutrients, but also can be used as an organic fertilizer.

(d) Organic fertilizer sources

1. **Animal:** Animal-sourced and human urea are suitable for application in organic agriculture, while pure synthetic forms of urea are not. The common object that can be seen through these examples is that organic agriculture attempts to define itself through minimal processing (in contrast to the man-made Haber process), as well as being naturally occurring or via natural biological processes such as composting.
2. **Plant:** Leguminous cover crops are also grown to enrich soil as a green manure through nitrogen fixation from the atmosphere, as well as phosphorus content of soils.

3. **Mineral:** Mined powdered limestone, rock phosphate and sodium nitrate are inorganic compounds which are energetically intensive to harvest and are approved for usage in organic agriculture in minimal amounts.

10.12 NEGATIVE ENVIRONMENTAL EFFECTS

Eutrophication

The nitrogen-rich compounds found in fertilizer runoff is the primary cause of a serious depletion of oxygen in many parts of the ocean, especially in coastal zones; the resulting lack of dissolved oxygen is greatly reducing the ability of these areas to sustain oceanic fauna.

Blue baby syndrome

High application rates of inorganic nitrogen fertilizers in order to maximize crop yields, combined with the high solubilities of these fertilizers, leads to increased runoff into surface water as well as leaching into ground water. The use of ammonium nitrate in *inorganic fertilizers* is particularly damaging, as plants absorb ammonium ions preferentially over nitrate ions, while excess nitrate ions which are not absorbed dissolve (by rain or irrigation) into run off or ground water.

Soil acidification

Nitrogen-containing inorganic and organic fertilizers can cause soil acidification. This may lead to decrease in nutrient availability.

Heavy metal accumulation

The concentration of up to 100 mg/kg of cadmium in phosphate minerals increases the contamination of soil with cadmium. Steel industry wastes, recycled into fertilizers for their high levels of zinc (essential to plant growth), can include the toxic metals: lead, arsenic and cadmium. The most common toxic elements in this type of fertilizer are mercury, lead, and arsenic.

Radioactive element accumulation

Uranium is another example of a contaminant often found in phosphate fertilizers. Also, highly radioactive Polonium-210 contained in phosphate fertilizers is absorbed by the roots of plants and stored in its tissues; tobacco derived from plants fertilized by rock phosphates contains Polonium-210 which emits alpha radiation estimated to cause lung cancer.

Atmosphere

Methane emissions from crop fields (notably rice paddy fields) are increased by the application of ammonium-based fertilizers; these emissions contribute greatly to global climate change as methane is a potent greenhouse gas. Through the increasing use of nitrogen fertilizer, nitrous oxide (N_2O) has become the third most important greenhouse gas after carbon dioxide and methane. It has a global warming potential 296 times larger than an equal mass of carbon dioxide and it also contributes to stratospheric ozone depletion. Ammonia gas (NH_3) may be emitted following application of 'inorganic' fertilizers and/or manures and slurries. The use of fertilizers on a global scale emits significant quantities of greenhouse gases into the atmosphere. Emissions come about through the use of:

- animal manures and urea, which release nitrous oxide, ammonia and carbon dioxide in varying quantities, and
- fertilizers that use nitric acid, the production and application of which results in emissions of nitrous oxide, ammonia and carbon dioxide into the atmosphere.

QUESTIONS

1. What are the differences between soil conditioners and fertilizers?
2. How does C:N ratio differ in various materials.
3. Give an idea about advantages and disadvantages in both aspects of soil conditioner.
4. How do you measure the physical properties of soil.
5. What are the six macronutrients and seven micronutrients provided by fertilizers?
6. What is the function of fertilizers?
7. Briefly describe the activities of soil conditioner.
8. Give an idea about the sources of fertilizers.

FURTHER READING

Baños, Philippines and Baños, Los (2000). Rice Research for Food Security and Poverty Alleviation. Proceedings of the International Rice Research Conference, International Rice Research Institute.

Barisic, D., Lulic, S. and Miletic, P. (1992). Radium and uranium in phosphate fertilizers and their impact on the radioactivity of waters. *Water Research*, **26(5):** 607-611.

Bodelier, Paul, L.E., Peter Roslev, Thilo Henckel and Peter Frenzel (1999). Stimulation by ammonium-based fertilizers of methane oxidation in soil around rice roots. *Nature,* **403(6768):** 421-424.

Erisman, Jan Willem, Sutton, M.A., Galloway, J., Klimont, Z. and Winiwarter, W. (2008). How a century of ammonia synthesis changed the world? *Nature Geoscience,* **1(10):** 636.

Fliessbach, A., Maeder, P., Diop, A., Luttikholt, L.W.M., Scialabba, N., Niggli, U., Hepperly, Paul and LaSalle, T. (2009). Climate Change: Global Risks, Challenges and Decisions. *In:* Mitigation and adaptation strategies – organic agriculture. IOP Conf. Series: Earth and Environmental Science 6(2009)242025: IOP Publishing.

Hussein, E.M. (1994). Radioactivity of phosphate ore, superphosphate, and phosphogypsum in Abu-zaabal phosphate. *Health Physics*, **67(3):** 280-282.

Jahn, G.C. (2004). Effect of soil nutrients on the growth, survival and fecundity of insect pests of rice: An overview and a theory of pest outbreaks with consideration of research approaches. Multitrophic interactions in Soil and Integrated Control. *International Organization for Biological Control (IOBC) Bulletin,* **27(1):** 115-122.

Jahn, G.C., Almazan, L.P. and Pacia, J. (2005). Effect of nitrogen fertilizer on the intrinsic rate of increase of the rusty plum aphid, *Hysteroneura setariae* (Thomas) (Homoptera: Aphididae) on rice (*Oryza sativa* L.). *Environmental Entomology*, **34(4):** 938-943.

Jahn, G.C., Cox, P.G., Rubia-Sanchez, E. and Cohen, M. (2001). The quest for connections: Developing a research agenda for integrated pest and nutrient management. *In:* S. Peng and B. Hardy (eds), International Rice Research Institute – Discussion Paper 42: 18.

Mills, H.A. and Jones Jr., J.B. (1996). Plant Analysis Handbook II: A practical Sampling, Preparation, Analysis, and Interpretation Guide. ISBN 1-878148-052.

Pimentel, David, Paul Hepperly, James Hanson, David Douds and Rita Seidel (2005). Environmental, Energetic, and Economic Comparisons of Organic and Conventional Farming Systems. *BioScience*, **55(7):** 573-582.

Preap, V., Zalucki, M.P. and Jahn, G.C. (2002). Effect of nitrogen fertilizer and host plant variety on fecundity and early instar survival of Nilaparvata lugens (Stål): Immediate response. Proceedings of the 4th International Workshop on Inter-Country Forecasting System and Management for Planthopper in East Asia. November 13-15, 2002. Guilin China. Published by Rural Development Administration (RDA) and the Food and Agriculture Organization (FAO): 163-180, 226.

Preap, V., Zalucki, M.P., Nesbitt, H.J. and Jahn, G.C. (2001). Effect of fertilizer, pesticide treatment, and plant variety on realized fecundity and survival rates of Nilaparvata lugens (Stål): Generating Outbreaks in Cambodia. *Journal of Asia Pacific Entomology*, **4(1):** 75-84. doi:10.1016/S1226-8615(08)60107-7.

Scholten, L.C. and Timmermans, C.W.M. (1992). Natural radioactivity in phosphate fertilizers. *Nutrient Cycling in Agroecosystems,* **43:** 103-107.

Stewart, W.M., Dibb, D.W., Johnston, A.E. and Smyth, T.J. (2005). The Contribution of Commercial Fertilizer Nutrients to Food Production. *Agronomy Journal*, **97:** 1-6.

Syers, J.K., Mackay, A.D., Brown, M.W. and Currie, C.D. (1986). Chemical and physical characteristics of phosphate rock materials of varying reactivity. *J Sci Food Agric,* **37(11):** 1057-1064.

Taylor, M.D. (1997). Accumulation of Cadmium derived from fertilizers in New Zealand soils. *Science of Total Environment*, **208:** 123-126.

Trueman, N.A. (1965). The phosphate, volcanic and carbonate rocks of Christmas Island (Indian Ocean). *J. Geol Soc Aust*, **12:** 261-286.

Vance, Uhde-Stone and Allan (2003). Phosphorus acquisition and use: Critical adaptations by plants for securing a non-renewable resource. *New Phythologist* (Blackwell Publishing), **157(3):** 423-447. doi:10.1046/j.1469-8137.2003.00695.x. JSTOR 1514050.

Wilson, Duff (1997). Fear in the Fields – How Hazardous Wastes Become Fertilizer – Spreading Heavy Metals on Farmland is Perfectly Legal, But Little Research has been Done to Find Out Whether It’s Safe. *Seattle Times*.

CHAPTER

11

USE OF CLAYS AS DRILLING FLUIDS AND FILTERS

11.1 DRILLING FLUIDS

In geotechnical engineering, drilling fluid is a fluid used to drill boreholes into the earth. In drilling rigs, drilling fluids help to do drill for exploration of oil and natural gas. Liquid drilling fluid is often called drilling mud. The three main categories of drilling fluids are:

Water-based mud: which can be dispersed and non-dispersed.
Non-aqueous mud: usually called oil-based mud.
Gaseous drilling fluid: in which a wide range of gases can be used.

The main functions of drilling fluids include providing hydrostatic pressure to prevent formation fluids from entering into the well bore, keeping the drill bit cool and clean during drilling, carrying out drill cuttings, and suspending the drill cuttings while drilling is paused and when the drilling assembly is brought in and out of the hole. The drilling fluid used for a particular job is selected to avoid formation damage and to limit corrosion.

11.2 TYPES OF DRILLING FLUID

Many types of drilling fluids are used on a day-to-day basis. Some wells require that different types be used at different parts in the hole, or that some types be used in combination with others. The various types of fluid generally fall into a few broad categories (Table 11.1).

On a drilling rig, mud is pumped from the *mud pits* through the drill string where it sprays out of nozzles on the drill bit, cleaning and cooling the drill bit in the process. The mud then carries the crushed or cut rock (“cuttings”) up the annular space (“annulus”) between the drill string and the sides of the hole

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Table 11.1: Brief descriptions of different drilling fluids

Drilling fluid	*Description*
Air	Compressed air is pumped either down the bore hole's annular space or down the drill string itself.
Air/water	The same as above, with water added to increase viscosity, flush the hole, provide more cooling, and/or to control dust.
Air/polymer	A specially formulated chemical, most often referred to as a type of polymer, is added to the water and air mixture to create specific conditions. A foaming agent is a good example of a polymer.
Water	Water by itself is sometimes used.
Water-based mud (WBM)	A most basic water-based mud system begins with water, then clays and other chemicals are incorporated into the water to create a homogenous blend resembling something between chocolate milk and a malt (depending on viscosity). The clay (called "shale" in its rock form) is usually a combination of native clays that are suspended in the fluid while drilling, or specific types of clay that are processed and sold as additives for the WBM system. The most common of these is bentonite, frequently referred to in the oilfield as "gel".
Oil-based mud (OBM)	Oil-based mud can be a mud where the base fluid is a petroleum product such as diesel fuel. Oil-based muds are used for many reasons, some being increased lubricity, enhanced shale inhibition, and greater cleaning abilities with less viscosity. Oil-based muds also withstand greater heat without breaking down. The use of oil-based muds has special considerations.
Synthetic-based fluid (SBM) (Otherwise known as Low Toxicity Oil Based Mud or LTOBM)	Synthetic-based fluid is a mud where the base fluid is a synthetic oil. This is most often used on offshore rigs because it has the properties of an oil-based mud, but the toxicity of the fluid fumes are much less than an oil-based fluid. This is important when men work with the fluid in an enclosed space such as an offshore drilling rig.

being drilled, up through the surface *casing,* where it emerges back at the surface. Cuttings are then filtered out with either a shale shaker, or the new shale conveyor technology, and the mud returns to the *mud pits*. The mud pits let the drilled "fines" settle; the pits are also where the fluid is treated by adding chemicals and other substances.

The returning mud can contain natural gases or other flammable materials which will collect in and around the shale shaker/conveyor area or in other work areas. Because of the risk of a fire or an explosion if they ignite, special monitoring sensors and explosion-proof certified equipment is commonly installed, and workers are advised to take safety precautions. The mud is then pumped back down the hole and further re-circulated. After testing, the mud is

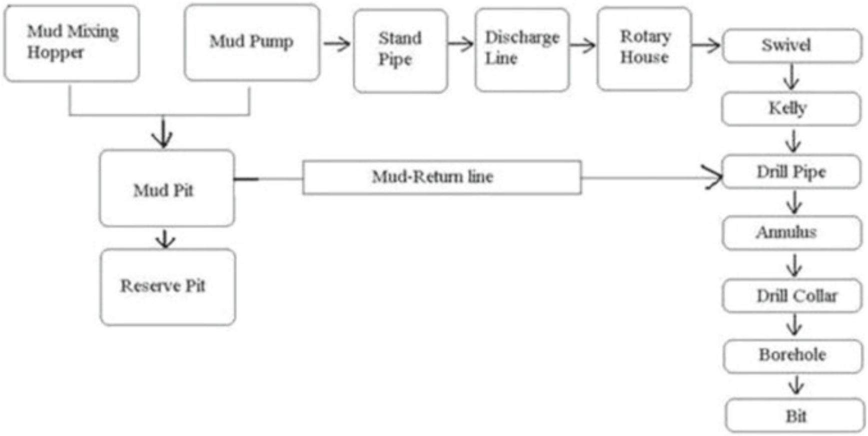

Fig. 11.1: Flow chart of drilling process.

treated periodically in the mud pits to ensure properties which optimize and improve drilling efficiency, borehole stability, and other requirements listed below.

11.3 FUNCTION

The main functions of a *drilling mud* can be summarized as follows:

(a) Remove Cuttings from Well

Drilling fluid carries the rock excavated by the drill bit up to the surface. Its ability to do so depends on cutting size, shape and density, and speed of fluid travelling up the well (annular velocity). These considerations are analogous to the ability of a stream to carry sediment; large sand grains in a slow-moving stream settle to the stream bed, while small sand grains in a fast-moving stream are carried along with the water.

Other properties include:

- Higher annular velocity improves cutting transport. Transport ratio (transport velocity/lowest annular velocity) should be at least 50%.
- High density fluids may clean hole adequately even with lower annular velocities (by increasing the buoyancy force acting on cuttings). But it may have a negative impact if mud weight is in excess of that needed to balance the pressure of surrounding rock (formation pressure), so mud weight is not usually increased for hole cleaning purposes.
- Higher rotary drill-string speeds introduce a circular component to annular flow path. This helical flow around the drill-string causes drill cuttings near the wall, where poor hole cleaning conditions occur, to move into higher transport regions of the annulus. Increased rotation are the best methods in high angle and horizontal beds.

(b) Suspend and Release Cuttings

- Must suspend drill cuttings, weight materials and additives under a wide range of conditions.
- Drill cuttings that settle can cause bridges and fill, which can cause stuck-pipe and lost circulation.
- Weight material that settles is referred to as sag; this causes a wide variation in the density of well fluid, which occurs more frequently in high angle and hot wells.
- High concentrations of drill solids are detrimental to:
  - Drilling efficiency (it causes increased mud weight and viscosity, which in turn increases maintenance costs and increased dilution)
  - Rate of Penetration (ROP) (increases horsepower required to circulate)

(c) Control Formation Pressures

- If formation pressure increases, mud density should also be increased, often with barite (or other weighting materials) to balance pressure and keep the well-bore stable. Unbalanced formation pressures will cause an unexpected influx of pressure in the well-bore; possibly leading to a blowout from pressured formation fluids.
- Hydrostatic pressure = density of drilling fluid × true vertical depth * acceleration of gravity. If hydrostatic pressure is greater than or equal to formation pressure, formation fluid will not flow into the well-bore.
- Well control means no uncontrollable flow of formation fluids into the well-bore.
- Hydrostatic pressure also controls the stresses caused by tectonic forces. These may make well-bores unstable even when formation fluid pressure is balanced.
- If formation pressure is subnormal, air, gas, mist, stiff foam, or low density mud (oil base) can be used.

(d) Seal Permeable Formations

- When mud column pressure exceeds formation pressure, mud filtrate invades the formation, and a filter cake of mud is deposited on the well-bore wall.
- Mud is designed to deposit thin, low permeability filter cake to limit the invasion.
- Problems occur if a thick filter cake is formed in tight hole conditions, poor log quality, stuck pipe, lost circulation and formation damage.
- In highly permeable formations with large pore throats, whole mud may invade the formation, depending on mud solids size.

  - Use bridging agents to block large opening, then mud solids can form seal.
  - For effectiveness, bridging agents must be over the half size of pore spaces/fractures.
  - Bridging agents (e.g. calcium carbonate, ground cellulose).
- ➜ Depending on the mud system in use, a number of additives can improve the filter cake (e.g. bentonite, natural and synthetic polymer, asphalt and gilsonite).

11.4 MAINTAIN WELL-BORE STABILITY

- Well-bore instability = sloughing formations, which can cause tight hole conditions, bridges and fill on trips (same symptoms indicate hole cleaning problems).
- Well-bore stability = hole maintains size and cylindrical shape.
- Chemical composition and mud properties must combine to provide a stable well-bore. Weight of the mud must be within the necessary range to balance the mechanical forces.
- If the hole is enlarged, it becomes weak and difficult to stabilize, resulting in problems such as low annular velocities, poor hole cleaning, solids loading and poor formation evaluation.
- In sand and sandstones formations, hole enlargement can be accomplished by mechanical actions (hydraulic forces and nozzles velocities). Formation damage is reduced by conservative hydraulics system. A good quality filter cake containing bentonite is known to limit bore-hole enlargement.
- In shales, mud weight is usually sufficient to balance formation stress, as these wells are usually stable. With water based mud, chemical differences can cause interactions between mud and shale that lead to softening of the native rock. Highly fractured, dry, brittle shales can be extremely unstable (leading to mechanical problems).
- Oil (and synthetic oil) based drilling fluids are used to drill most water sensitive shales in areas with difficult drilling conditions.

11.5 MINIMIZING FORMATION DAMAGE

- ➜ Most common damage:
  - Mud or drill solids invade the formation matrix, reducing porosity and causing skin effect
  - Swelling of formation clays within the reservoir, reduced permeability
  - Precipitation of solids due to mixing of mud filtrate and formations fluids resulting in the precipitation of insoluble salts
  - Mud filtrate and formation fluids form an emulsion, reducing reservoir porosity

- Specially designed drill-in fluids or workover and completion fluids, minimize formation damage.

11.6 COOL, LUBRICATE AND SUPPORT THE BIT AND DRILLING ASSEMBLY

- Cool and transfer heat away from source and lower to temperature than bottom hole.
- If not, the bit, drill string and mud motors would fail more rapidly.
- Lubrication based on the coefficient of friction. Oil- and synthetic-based mud generally lubricate better than water-based mud (but the latter can be improved by the addition of lubricants).
- Heat is generated from mechanical and hydraulic forces at the bit and when the drill string rotates and rubs against casing and well-bore.
- Amount of lubrication provided by drilling fluid depends on type and quantity of drill solids and weight materials and chemical composition of system.
- Poor lubrication causes high torque and drag, heat checking of the drill string, but these problems are also caused by key seating, poor hole cleaning and incorrect bottom hole assemblies design.
- Drilling fluids also support portion of drill-string or casing through buoyancy. Suspend in drilling fluid, buoyed by force equal to weight (or density) of mud, so reducing hook load at derrick.
- Weight that derrick can support is limited by mechanical capacity; increase depth so weight of drill-string and casing increases.

11.7 ENSURE ADEQUATE FORMATION EVALUATION

- Chemical and physical mud properties and well-bore conditions after drilling affect formation evaluation.
- Potential productive zone are isolated and performed formation testing and drill stem testing.
- Mud helps not to disperse of cuttings and also improve cutting transport for mud loggers determine the depth of the cuttings originated.
- Oil-based mud, lubricants and asphalts will mask hydrocarbon indications.
- So mud for drilling core is selected based on type of evaluation to be performed (many coring operations specify a blend mud with minimum of additives).

11.8 CONTROL CORROSION (at Acceptable Level)

- Drill-string and casing in continuous contact with drilling fluid may cause a form of corrosion.
- Dissolved gases (oxygen, carbon dioxide, hydrogen sulfide) cause serious corrosion problems:

  - Cause rapid, catastrophic failure
  - May be deadly to humans after a short period of time
- Low pH (acidic) may be the cause of corrosion and aggravates, so ‘corrosion coupon’ is essential to monitor the type of corrosion and simultaneously can suggest the right material (chemical inhibitor) to resist it.
- Mud aeration, foaming and other O_2 trapped conditions cause corrosion damage in short period time.
- When drilling in high H_2S, elevate the pH fluids + sulphide scavenging chemical (zinc).

11.9 FACILITATE CEMENTING AND COMPLETION

- Cementing is critical to effective zone and well completion.
- During casing run, mud must remain fluid and minimize pressure surges so fracture induced lost circulation do not occur.
- Mud should have thin, slick filter cake, well-bore with no cuttings, cavings or bridges.
- To cement and complete operation properly, mud is displaced by flushes and cement.

11.10 COMPOSITION OF DRILLING MUD

Water-based drilling mud most commonly consists of bentonite clay (gel) with additives such as barium sulphate (barite), calcium carbonate (chalk) or hematite. Various thickeners are used to influence the viscosity of the fluid, e.g. guar gum, glycol, carboxy methylcellulose, polyanionic cellulose (PAC), or starch. In turn, deflocculants are used to reduce viscosity of clay-based muds; anionic polyelectrolytes (e.g. acrylates, polyphosphates, lignosulphonates (Lig) or tannic acid derivates such as Quebracho) are frequently used. Red mud was the name for a Quebracho-based mixture, named after the colour of the red tannic acid salts. Some other common additives include lubricants, shale inhibitors and fluid loss additives (to control loss of drilling fluids into permeable formations). A weighting agent such as barite is added to increase the overall density of the drilling fluid so that sufficient bottom hole pressure can be maintained.

11.11 USE OF CLAYS AS FILTERS

Filtering is the screening processes for removal of contaminants present in a bulk sample. Due to its adsorption properties and large surface area, clays have enormous use as filters. With the addition of suitable organic substances, the adsorption properties can be altered. Such synthetically produced clays are called inorgano-organo clays. To remove pollutants these clays have wide applications, some of them are described below.

To purify water, use of clay pots is a very well known old process. With time, variation of filtering materials and methods have been developed as needed. This purification process of water varies according to the scale of purification and also the amount and type of contaminants present e.g. the water purification for household need is quite different from the waste water purification processes or removal of oils and fat or colour contaminants. The purification of waste water from various industries is an acute problem. To tackle such widely varied problems, clays with a combination of suitable organic compounds were synthetically developed to alter the filtering properties and processes as needed.

A brief division of filtering using clay types are: (1) Water filtration for household purpose, (2) Large scale filtration for waste waters from Industry and sewerage, (3) Desalination of water, (4) Use of bleaching clays in processing edible oils and (5) Filter materials for smoking items like cigars etc. to reduce health hazard problems.

11.12 WATER FILTRATION FOR HOUSEHOLD PURPOSE

These filters produce small amounts of water per day to meet the daily needs of 25 to 30 litres per person. Use of clay pot filters is a very well known old process.

Clay-saw Dust Filter

A paste with mixture of the clay and saw dust (of about 20 micron size) with different proportions (depending on the plasticity of clay used) is given the needed shape and fired to make it hard porous solid ready for filtration. This very simple type filter can only filter out the particles and colour out of water but is unable to remove bacteria.

Ceramic Water Filters (CWF)

These rely on the small pore size of the ceramic material, are inexpensive and more effective water filter, to filter dirt, debris, and bacteria, protozoa, and microbial cyst etc. out of water. But again, this is not effective against viruses since they are of smaller size than the pores and can pass through to the other "clean" side of the filter. To overcome this, CWF are treated with silver in a form that will not leach away helps to kill or incapacitate bacteria and prevent the growth of algae in the body of the filter.

A high-performance activated carbon core inside the ceramic filter cartridge is used that reduces organic and metallic contaminants and some chemical compounds such as chlorine etc. for the absorbing property of Active Carbon. These filters need to be replaced periodically because the carbon becomes clogged with foreign material.

CWF systems consist of a porous ceramic filter that sits on top of a plastic or ceramic receptacle. Contaminated water is to pass through the filter into the receptacle below. The receptacle usually is fitted with a tap.

When used to treat turbid water, the filter needs to be frequently scrubbed clean to remove the retained material. This abrasive treatment rapidly wears away the ceramic. Care has to be taken to prevent cracking of the ceramic as short circuiting of the filter by pathogens can occur.

Main risks to the success of all forms of CWF are hairline cracks and cross-contamination. If the unit is dropped or otherwise abused, the brittle nature of ceramic materials can allow fine, hard to see hairline cracks, and pass contaminants through the filter.

11.13 LARGE SCALE FILTRATION FOR PURIFYING WATER

Removal of contaminations from the waste waters (from different Industries, sewerage etc.)

Removal of even trace level of pollutants from very large volume of waste water is a micro separation process. For such applications, the adsorbents need to be cost effective.

Clay adsorbents are modified by combining organic substances, produced synthetically, and these inorgano-organo clays are of vital importance to remove pollutants from industrial waste water. The basic material of inorganic clay phase is varieties of expanding clays, like montmorrilonite, bentonite etc.

Removal of Coloured Organics from Aqueous Solutions

For removing the coloured organic substances in various aqueous systems, use of Anion Clay Hydrocalcite is a very effective method. The coloured substances can be adsorbed on the surface or enter the inter-layer region of clay by anion exchange. Adsorption capacity of hydro calcite is a little more than the commercially activated carbon. By heating at 723°K all the adsorbed organics can be removed and the used sorbent can be reused again with greater adsorbing capacity. This sorbent is becoming very useful and environmental friendly for water purification process.

Removal of Oils from Contaminated Water

For oil removal, use of organoclay is used in water treatment technology since 1995. Organo clays are developed using basically bentonite clays (mostly montmorillonite) mixing with quaternary amines (organic compounds derived from ammonia (NH_3), where the hydrogen atom is replaced by CH_3 or CH_5) under suitable temperature and pressure and pH-conditions. This modified bentonites or other organo clays are used (as filter candles or granules) to remove the oils, grease or other sparingly soluble organics from water.

11.14 DESALINATION OF WATER (in Large Scale)

To make saline water usable, removal of salinity is essential. This is called desalination and during this process some other minerals are also removed. The methods of desalination are listed below.

Distillation

Three types of distillation processes are used to desalinate water, but none of them use clay. These three methods are:

(i) **Multistage Flash Distillation** (MSF): Almost 85% of world's desalinated sea water is obtained using this method. This is essentially a countercurrent heat exchange process where flashing a portion of the water into steam in multiple stages distillation is processed.

(ii) **Multiple-effect Distillation** (MED): In this process, repeated distillation of the feed water system through tubes is performed. These tubes are either submerged inside or the feed water is being spread on the steam tubes. Evaporation of water by steam in multiple stages ensures increased volume of distilled water which is collected from the bottom of the distillation apparatus.

(iii) **Vapour Compression:** It is a distillation process where the heat is supplied by compressed vapour. In this method, the latent heat of the vapour is used during condensation to get extra heat (compression of the vapour increases both pressure and temperature).

Ion Exchange

These processes are widely used for water purification, decontamination and water softening. Being a reversible process, the ion exchanger can be reused with desirable ions.

Use of Membranes

Separation/desalination/purification using membranes is essentially a mechanical process and usually no heating is needed but sometime operates using pressure, thus consumes less energy. The main division of this method are: (i) Electro-Dialysis Reversal (EDR), (ii) Reverse Osmosis (RO), (iii) Nano-Filtration (NF) and (iv) Membrane Distillation.

11.15 USE OF BLEACHING CLAYS IN PROCESSING EDIBLE OILS

For bleaching of oils and fats, bentonite clays are used. These commercial bleaching clays are of two types e.g. natural (bentonites) and activated (montmorrilonites of suitably enriched ions by chemical processing) clays. The bleaching clays are intimately mixed with oils for specified time and predecided temperature with suitable agitation conditions. This bleaching process may need repeated operating cycles for desirable result. The used clay will be precipitated at the bottom of the chamber and can be reused. The oil will be collected in a different chamber.

11.16 FILTER MATERIALS FOR SMOKING ITEMS LIKE CIGARS

For reducing the harmful content of tobacco smoke filters are used. Filter materials are produced using a suitable mixture of clays with zeolites and used in cigarettes, cigars, tobacco pipes, cigar holders etc. Clays have enormous uses as filters due to its adsorption properties and large surface area.

QUESTIONS

1. Give a schematic diagram on flow chart of drilling process.
2. What are the types of drilling agent?
3. Choosing of drilling agent, how does it depend on pressure.
4. How can the formation damage be minimized.
5. What are the usages of filter?
6. Explain the following terms:
   Shortpass, Longpass, Bandpass, Dichroic filter, Absorptive.

FURTHER READING

Alther, George R. (1995). Organically modified clay removes oil from water. *Waste Management*, **15:** 623-628.

ASME Shale Shaker Committee (2005). The Drilling Fluids Processing Handbook. ISBN: 0-7506-7775-9.

Chilingarian, G.V. and Vorabutr, P. (1983). Drilling and Drilling Fluids. Elsevier.

Gray, G.R., Darley, H.C.H. and Rogers, W.F. (1980). The Composition and Properties of Oil Well Drilling Fluids. Gulf Pub. Co., Houston.

Greenlee, L.F., Lawler, D.F., Freeman, B.D. and Marrot, B. (2009). Desalination Plant and Water Technology. *Water Research*, **43(9):** 2317-2348.

Kate Van Dyke (1998). Drilling Fluids, Mud Pumps and Conditioning Equipment. ISBN: 10-0886981816.

Orthman, J., Zhu, H.Y. and Lu, G.Q. (2003). Use of Anion Clay...Aqueous Solutions. *Separation and Purification Technology*, **31(1):** 53-59.

Richardson, Louise I. (1950). Use of bleaching clays in processing edible oils. W Century Building, Los Alamos, CA 90045.

Srinivasan, K.R., Fogler, H.S. et al. (1985). Clays and Clay Minerals. Elsevier.

CHAPTER

12

CLAYS AND ASSOCIATED MATERIALS IN SURFACE COATINGS AND PIGMENTS

12.1 PURPOSE OF SURFACE COATINGS

Coating indicates a covering applied to the surface of an object. In many cases, coatings are applied to improve surface properties of the substrate, such as appearance, adhesion and resistance against any type of corrosion or weathering. In other cases, coating forms an essential part of the finished product. Coatings may be applied as liquids, gases or solids. Surface coating—any mixture of film-forming materials plus pigments, solvents and other additives—when applied to a surface and cured or dried, yields a thin film that is functional and often decorative. Surface coatings include paints, drying oils and varnishes, synthetic clear coatings, and other products whose primary function is to protect the surface of an object from the environment. These products can also enhance the aesthetic appeal of an object by accentuating its surface features or even by concealing them from view. Most surface coatings employed in industry and by consumers are based on synthetic polymers, that is, industrially produced substances composed of extremely large, often interconnected, molecules that form tough, flexible, adhesive films when applied to surfaces. The other component materials of surface coatings are pigments, which provide colour, opacity, gloss and other properties; solvents or carrier liquids which provide a liquid medium for applying the film-forming ingredients; and additives which provide a number of special properties.

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Table 12.1: Functions of surface coatings

Properties	*Functions*
Melt-adhesive properties	For vacuum seal and heat seal applications
"Release" coatings	The liner of a double-sided tape or vinyl stickers
Low surface energy coatings	To act as a non-stick surface
Photo-sensitivity	For photographic film and paper
Water proofing coatings	For fabrics or paper, or on wood surfaces such as outdoor furniture, patio decks, yacht hulls and decks
Self adhesive properties	For tape, labels and packaging
Optical properties	Tint, colour, anti-reflection and holographic
Electronic properties	Passivity or conduction as with flexible circuits
Magnetic properties	For magnetic media like cassette tapes and floppy disks

12.2 CHEMICAL VAPOUR DEPOSITION

The chemical vapour deposition is discussed here as Metalorganic vapour phase epitaxy and Electrostatic spray assisted vapour deposition.

Metalorganic Vapour Phase Epitaxy

Metalorganic vapour phase epitaxy (MOVPE), also known as organometallic vapour phase epitaxy (OMVPE) or metalorganic chemical vapour deposition (MOCVD), is a chemical vapour deposition method of epitaxial growth of materials, especially compound semiconductors, from the surface reaction of organic compounds or metalorganics and metal hydrides containing the required chemical elements. For example, indium phosphide could be grown in a reactor on a substrate by introducing trimethylindium ($(CH_3)_3In$) and phosphine (PH_3). Formation of the epitaxial layer occurs by final pyrolysis of the constituent chemicals at the substrate surface.

Electrostatic Spray Assisted Vapour Deposition

Electrostatic spray assisted vapour deposition (ESAVD) is a technique to deposit both thin and thick layers of a coating on to various substrates. In simple terms when chemical precursors are sprayed across an electrostatic field towards a heated substrate, the chemicals undergo a controlled chemical reaction and are deposited on the substrate as the required coating. Electrostatic spraying techniques were developed in the 1950s for the spraying of ionized particles on charged or heated substrates.

ESAVD (branded by IMPT as Layatec) is used for various applications in many markets including:

- Thermal barrier coatings for jet engine turbine blades
- Electronic components

- Glass coatings (such as self cleaning)
- Corrosion protection coatings

12.3 PHYSICAL VAPOUR DEPOSITION

Physical vapour deposition (PVD) is a variety of vacuum deposition and is a general term used to describe any of a variety of methods to deposit thin films by the condensation of a vapourized form of the desired film material on to various workpiece surfaces (e.g., on to semiconductor wafers). The coating method involves purely physical processes such as high temperature vacuum evaporation with subsequent condensation, or plasma sputter bombardment rather than involving a chemical reaction at the surface to be coated as in chemical vapour deposition.

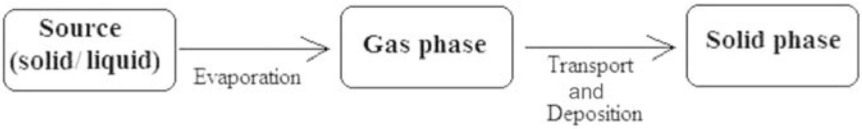

Fig. 12.1: Process flow diagram.

PVD is used in the manufacture of items including semiconductor devices, aluminized PET film for balloons and snack bags, and coated cutting tools for metalworking. Besides PVD tools for fabrication, special smaller tools mainly for scientific purposes have been developed. They mainly serve the purpose of extreme thin films like atomic layers and are used mostly for small substrates. A good example are mini e-beam evaporators which can deposit monolayers of virtually all materials with melting points up to 3500°C. The source material is unavoidably also deposited on most other surfaces interior to the vacuum chamber, including the workholders.

Table 12.2: Some techniques to measure the physical properties of PVD coatings

Techniques	*Purpose*
Calo tester	Coating thickness test
Pin on disc tester	Wear and friction coefficient test
Nanoindentation	Hardness test for thin-film coatings
Scratch tester	Coating adhesion test

12.4 CHEMICAL AND ELECTROCHEMICAL TECHNIQUES

Anodizing

Anodizing, or anodizing, is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal parts. The process is called "anodizing" because the part to be treated forms the anode electrode of an electrical circuit. Anodizing increases corrosion resistance and wear resistance, and provides better adhesion for paint primers and glues than does bare metal. Anodic films can also be used for a number of cosmetic effects, either with thick porous coatings that can absorb dyes or with thin transparent coatings that add interference effects to reflected light. Anodizing is also used to prevent galling of threaded components and to make dielectric films for electrolytic capacitors. Anodic films are most commonly applied to protect aluminium alloys, although processes also exist for titanium, zinc, magnesium, niobium and tantalum. Iron or carbon steel metal exfoliates when oxidized under neutral or alkaline microelectrolytic conditions; i.e., the iron oxide (actually "ferric hydroxide" or hydrated iron oxide, also known as rust) is formed by anoxic anodic pits and large cathodic surface. These pits concentrate anions such as sulfate and chloride accelerating the underlying metal to corrosion. Carbon flakes or nodules in iron or steel with high carbon content (high carbon steel, cast iron) may cause an electrolytic potential and interfere with coating or plating. Ferrous metals are commonly anodized electrolytically in nitric acid, or by treatment with red fuming nitric acid, to form hard black ferric oxide. This oxide remains conformal even when plated on wire and the wire is bent. Anodization changes the microscopic texture of the surface and changes the crystal structure of the metal near the surface. Thick coatings are normally porous, so a sealing process is often needed to achieve corrosion resistance.

Conversion Coatings

Conversion coatings are coatings for metals where the part surface is converted into the coating with a chemical or electro-chemical process. Examples include chromate conversion coatings, phosphate conversion coatings, bluing, black oxide coatings on steel, and anodizing. They are used for corrosion protection, increased surface hardness, to add decorative colour and as paint primers. Conversion coatings may be very thin, of the order of 0.00001″. Thick coatings, up to 0.002″, are usually built up on aluminium alloys, either by anodizing or chromate conversion.

Ion Beam Mixing

It is a process for adhering two multilayers, especially a substrate and deposited surface layer. The process involves bombarding layered samples with doses of ion radiation in order to promote mixing at the interface, and generally serves as a means of preparing electrical junctions, especially between non-equilibrium or metastable alloys and intermetallic compounds. Ion implantation equipment can be used to achieve ion beam mixing.

Tarnision

It is a metal surface treatment used to remove impurities, such as stains, inorganic contaminants, rust or scale from ferrous metals, copper and aluminum alloys. A solution called tarnision liquor, which contains strong acids, is used to remove the surface impurities. It is commonly used to descale or clean steel in various steelmaking processes.

Plating

It is a surface covering in which a metal is deposited on a conductive surface. Plating has been done for hundreds of years, but it is also critical for modern technology. Plating is used to decorate objects, for corrosion inhibition, to improve solderability, to harden, to improve wearability, to reduce friction, to improve paint adhesion, to alter conductivity, for radiation shielding, and for other purposes. Jewellery typically uses plating to give a silver or gold finish. Thin-film deposition has plated objects as small as an atom; therefore plating finds uses in nanotechnology. There are several plating methods, and many variations. In one method, a solid surface is covered with a metal sheet, and then heat and pressure are applied to fuse them (a version of this is Sheffield plate). Other plating techniques include vapour deposition under vacuum and sputter deposition. Recently, plating often refers to using liquids. Metallizing refers to coating metal on non-metallic objects.

Sol-gel

The sol-gel process is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically metal oxides) starting from a colloidal solution (sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal salts (such as chlorides, nitrates and acetates), which undergo various forms of hydrolysis and polycondensation reactions.

12.5 SPRAYING

Thermal Spraying

Thermal spraying techniques are coating processes in which melted (or heated) materials are sprayed on to a surface. Thermal spraying can provide thick coatings (approx. thickness range is 20 micrometres to several mm, depending on the process and feedstock), over a large area at high deposition rate as compared to other coating processes such as electroplating, physical and chemical vapour deposition. Coating materials available for thermal spraying include metals, alloys, ceramics, plastics and composites. They are fed in powder or wire form, heated to a molten or semimolten state and accelerated towards substrates in the form of micrometre-size particles. Combustion or electrical arc discharge is usually used as the source of energy for thermal spraying. Resulting coatings are made by the accumulation of numerous sprayed particles. The surface may not heat up significantly, allowing the coating of flammable substances. Coating quality is usually assessed by measuring its porosity, oxide content, macro- and micro-hardness, bond strength and surface roughness. Generally, the coating quality increases with increasing particle velocities.

Several variations of thermal spraying are: Plasma spraying; Detonation spraying; Wire arc spraying; Flame spraying; High velocity oxy-fuel coating spraying (HVOF); Warm spraying; and Cold spraying.

Plasma Spraying

In plasma spraying process, the material to be deposited typically as a powder, sometimes as a liquid, suspension or wire, is introduced into the plasma jet, emanating from a plasma torch. In the jet, where the temperature is of the order of 10,000 K, the material is melted and propelled towards a substrate. There the molten droplets flatten, rapidly solidify and form a deposit. Commonly, the deposits remain adherent to the substrate as coatings; free-standing parts can also be produced by removing the substrate. There are a large number of technological parameters that influence the interaction of the particles with the plasma jet and the substrate and therefore the deposit properties. These parameters include feedstock type, plasma gas composition and flow rate, energy input, torch offset distance, substrate cooling, etc.

12.6 OPTICAL COATING

An optical coating is one or more thin layers of material deposited on an optical component such as a lens or mirror, which alters the way in which the optic reflects and transmits light. One type of optical coating is an antireflection coating, which reduces unwanted reflections from surfaces, and is commonly used on spectacle and photographic lenses. Another type is the high-reflector coating which can be used to produce mirrors which reflect greater than 99.99% of the light which falls on them. More complex optical coatings exhibit high reflection over some range of wavelengths, and anti-reflection over another range, allowing the production of dichroic thin-film optical filters.

12.7 CHARACTERISTICS OF PIGMENTS

A pigment is a material that changes the colour of reflected or transmitted light as a result of wavelength-selective absorption. This physical process differs from fluorescence, phosphorescence, and other forms of luminescence, in which a material emits light. Many materials selectively absorb certain wavelengths of light. Materials that humans have chosen and developed for use as pigments usually have special properties that make them ideal for colouring other materials. A pigment must have a high tinting strength relative to the materials it colours. It must be stable in solid form at ambient temperatures. Pigments are used for colouring paint, ink, plastic, fabric, cosmetics, food and other materials. Most pigments used in manufacturing and the visual arts are dry colourants, usually ground into a fine powder. This powder is added to a vehicle (or binder), a relatively neutral or colourless material that suspends the pigment and gives the paint its adhesion.

12.8 CONSTITUENTS OF PIGMENTS

The iron oxides minerals which form the major constituents of pigments are hematite, magnetite and goethite. Limonite, often used in the description of pigments, is a hydrated iron oxide of poor crystallinity and consists mainly of goethite or lepidocrocite.

Table 12.3: Physical properties of iron oxides and hydroxides minerals

Mineral	*Hardness*	*Specific gravity*	*Refractive index*	*Colour*
Hematite	5-6	5.25	2.87-3.22	Light red to dark violet
Goethite	5-5.50	4.3	2.26-2.51	Green yellow to brown yellow
Lepidocrocite	5	4.09	1.94-2.51	Yellow to orange
Magnetite	7.50-8	5.20	2.42	Black
Maghemite	7.50-8	4.88	2.52-2.74	Brown to orange brown

12.9 PHYSICAL BASIS

Pigments appear in the colours they are because they selectively reflect and absorb certain wavelengths of visible light. White light is a roughly equal mixture of the entire spectrum of visible light with a wavelength in a range from about 380 or 400 nanometres to about 760 or 780 nm. When this light encounters a pigment, parts of the spectrum are absorbed by the chemical bonds of conjugated systems and other components of the pigment. Some other

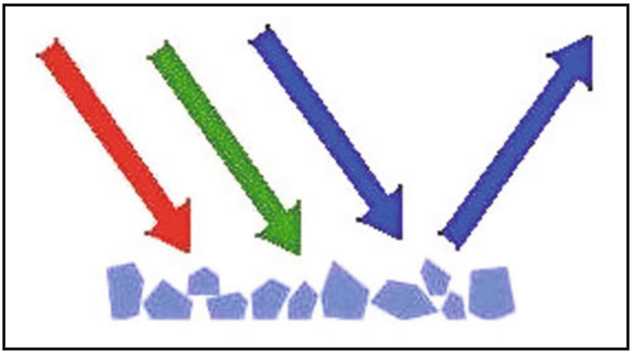

Fig. 12.2: A wide variety of wavelengths (colours) encounter a pigment. This pigment absorbs red and green lights, but reflects blue, creating the colour blue.

wavelengths or parts of the spectrum are reflected or scattered. Most pigments are charge transfer complexes, like transition metal compounds, with broad absorption bands that subtract most of the colours of the incident white light. The new reflected light spectrum creates the appearance of a colour. Ultramarine reflects blue light, and absorbs other colours. Pigments, unlike fluorescent or phosphorescent substances, can only subtract wavelengths from the source light, never add new ones. So a *blue pigment* is *blue* because it doesn't reflect *red* and *green* lights, or because it reflects all colours but the complementary of the *blue* one, which is *orange*. The appearance of pigments is intimately connected to the colour of the source light. Sunlight has a high colour temperature, and a fairly uniform spectrum, and is considered a standard for white light. Artificial light sources tend to have great peaks in some parts of their spectrum, and deep valleys in others. Viewed under these conditions, pigments will appear different colours.

Colour spaces used to represent colours numerically must specify their light source. Lab colour measurements, unless otherwise noted, assume that the measurement was taken under a D65 light source, or "Daylight 6500 K", which is roughly the colour temperature of sunlight.

Other properties of a colour, such as its saturation or lightness, may be determined by the other substances that accompany pigments. Binders and fillers added to pure pigment chemicals also have their own reflection and absorption patterns, which can affect the final spectrum. Likewise, in pigment/binder mixtures, individual rays of light may not encounter pigment molecules, and may be reflected as it is. These stray rays of source light contribute to the saturation of the colour. Pure pigment allows very little white light to escape, producing a highly saturated colour. A small quantity of pigment mixed with a lot of white binder, however, will appear desaturated and pale, due to the high quantity of escaping white light.

12.10 MANUFACTURING AND INDUSTRIAL STANDARDS

Before the development of synthetic pigments, and the refinement of techniques for extracting mineral pigments, batches of colour were often inconsistent. With the development of a modern colour industry, manufacturers and professionals have cooperated to create international standards for identifying, producing, measuring, and testing colours. First published in 1905, the Munsell Colour System became the foundation for a series of colour models, providing objective methods for the measurement of colour. The Munsell system describes a colour in three dimensions—hue, value (lightness) and chroma (colour purity)—where chroma is the difference from gray at a given hue and value. Many manufacturers of paints, inks, textiles, plastics, and colours have voluntarily adopted the Colour Index International (CII) as a standard for identifying the pigments that they use in manufacturing particular colours. First published in 1925, and now published jointly on the web by the Society of Dyers and Colourists (United Kingdom) and the American Association of Textile Chemists and Colorists (USA), this index is recognized internationally as the authoritative reference on colourants. It encompasses more than 27,000 products under more than 13,000 generic colour index names.

12.11 ATTRIBUTES OF PIGMENTS

The following are some of the attributes of pigments that determine their suitability for particular manufacturing processes and applications:

- Lightfastness and sensitivity for damage from ultra violet light
- Heat stability
- Toxicity
- Tinting strength
- Staining
- Dispersion
- Opacity or transparency
- Resistance to alkalis and acids
- Reactions and interactions between pigments

12.12 BIOLOGICAL PIGMENTS

In biology, a pigment is any coloured material of plant or animal cells. Many biological structures, such as skin, eyes, fur and hair contain pigments (such as melanin). Animal skin colouration is often achieved with specialized cells called chromatophores, which in animals such as the octopus and chameleon can be controlled to vary the animal's colour. Many conditions affect the levels or nature of pigments in plant, animal, some protista, or fungus cells. For instance, Albinism is a disorder affecting the level of melanin production in animals. Pigmentation is used in organisms for many biological purposes including camouflage, mimicry, aposematism (warning), sexual selection and other forms of signalling, photosynthesis (in plants), as well as basic physical purposes such as protection from sunburn. Pigment colour differs from structural colour in that it is the same for all viewing angles, whereas structural colour is the result of selective reflection or iridescence, usually because of multilayer structures. For example, butterfly wings typically contain structural colour, although many butterflies have cells that contain pigment as well.

12.13 USING PIGMENTS

Add the pigment to the slip and sieve through a 120× mesh screen to ensure adequate dispersion. Depending on the use, pigments may be used straight and just mixed with water, but they are more commonly added as colourants in clay bodies and glazes. Some pigments are specifically formulated for clay bodies while some are not suitable at all. When used in clay, pigments are usually used in engobes and slips as a coating for clay rather than pigmenting the entire body.

When using pigments in glazes, usually in concentrations of 1-10%, a little more care must be taken because some pigment systems react with materials in a glaze. Some pigments are affected by the presence, or lack of, boron, zinc, calcium and magnesia. Manufacturers provide information on specific reactions. While most pigments can be used in both oxidation and reduction atmospheres, some are limited to certain maximum temperatures. Again, this information is available from manufacturer websites. To achieve a wider palette, most pigments can be mixed to achieve even more colours. The exception is that black pigments cannot be used to obtain shades of gray because blacks are made from a combination of several metallic oxides. If low percentages are used, the final colour is affected by the predominant oxide in the black pigment.

12.14 KAOLIN CLAY AND ITS FEATURES

Clay, mainly Kaolin is used in pigment to form it as a paste like material, by increasing its density. The important features of kaolin clay are its purity, high brightness, easy dispersion, accurate chemical composition and capacity to withstand high temperature.

Table 12.4: Physical properties of kaolin clay

Contents	*Percentage*
Moisture	1.37%
pH of 10% solution	7 to 8
Bulk density	0.47 g/cc
Oil absorption	35 to 40%
Water absorption	29.94%
Loss on ignition	12.10%

Table 12.5: Chemical composition of kaolin clay

Contents	*Percentage*
Al_2O_3	33.67%
SiO_2	50.40%
Fe_2O_3	1.28%
CaO	0.20%
TiO_2	1.50%
MgO	0.30%
Na_2O	0.12%
K_2O	3.00%

12.15 SOME TYPES OF PIGMENTS

Using clay some pigments are formed and they are differentiated according to their physical and chemical properties and uses. These are highlighted below.

Ultra Marine Blue Pigment

Kaolin clay acts as ingredients for forming ultramarine blue pigments, which has dark blue colour. Best quality ultramarine blue is used in all types of laundry while technical and industrial grades for applications in coating, cosmetic, ink and plastic pigments.

High Whiteness Pigment

Calcined kaolin clay acts as ingredients, used in formation of washing powder and liquid blue. It is composed of Fe_2O_3, Al_2O_3, TiO_2 and moisture content. Whiteness and fine particles are main two characteristic features of it. Percentage of physical property and chemical composition are listed in Table 12.6.

Table 12.6: Chemical composition and physical properties of high whiteness pigments

Chemical compositions (%)		*Physical property (%)*	
Al_2O_3	36	Particle size -2 μm	70-75
TiO_2	0.2	Particles >45 μm	0.05
Fe_2O_3	0.75	Whiteness (%)	85
pH	4.0-6.0	Moisture (%)	2

N0842, Kaolin Clay Powder for Pigment

Main ingredients of formation of this type of pigments are kaolin clay. It is the best pigment, extender and filler in water-based coating. It is used in paper formation.

Table 12.7: Chemical components and percentage of kaolin clay

Chemical component	*Percentage of component*
Al_2O_3 content	32-38%
Moisture content	7-27%
TiO_2 content	<0.5%
K_2O content	<0.05%
Whiteness	85

China Clay

It is produced with calcined kaolin having high and standard brightness kaolin. It is used for paints, paper, plastics, rubber, pigments, fertilizers, pesticides, pharmaceuticals, cosmetics and medical.

Table 12.8: Chemical components and percentage of China clay

Chemical component	*Percentage of component*
SiO_2 content	45.8%
Fe_2O_3 content	0.21%
Al_2O_3 content	37.8%
Moisture content	1%
TiO_2 content	0.8%
K_2O content	0.065%
Whiteness	84-86

12.16 APPLICATIONS OF KAOLIN CLAY

- Used in paints for lending excellent exterior durability and archeological improvement
- Acts as an essential ingredient of oil-based and water-based paints
- Used as a coating pigment in the manufacture of coated paper and boards
- Demanded by the rubber industry to improve the impact resistance, tensile strength, hardness and abrasion of rubber
- Extensively used in PVC wires, inks, adhesives, toothpaste, soaps, etc.

QUESTIONS

1. How does functions of surface coatings relate with their properties.
2. What is physical vapour deposition? Explain with the help of diagram.
3. What are anodizing and spraying?
4. Briefly explain: attributes and constituents of pigments.
5. What are the various types of constituting clay and their percentage?
6. How does wavelength of colour influence the pigment?

FURTHER READING

Ball, Philip (2002). Bright Earth: Art and the Invention of Color. Farrar, Straus and Giroux. ISBN 0-374-11679-2.

Doerner, Max (1984). The Materials of the Artist and Their Use in Painting: With Notes on the Techniques of the Old Masters (Revised Edition). Harcourt. ISBN 0-15-657716-X.

Finlay, Victoria (2003). Color: A Natural History of the Palette. Random House. ISBN 0-8129-7142-6.

Gage, John (1999). Color and Culture: Practice and Meaning from Antiquity to Abstraction. University of California Press. ISBN 0-520-22225-3.

Greenfield, Amy Butler (2005). A Perfect Red: Empire, Espionage, and the Quest for the Color of Desire. HarperCollins. ISBN 0-06-052275-5.

Kassinger, Ruth G. (2003). Dyes: From Sea Snails to Synthetics. 21st Century. ISBN 0-7613-2112-8. http://books.google.com/books?visbn=0761321128.

Meyer, Ralph (1991). The Artist's Handbook of Materials and Techniques, Fifth Edition. Viking. ISBN 0-670-83701-6.

Pastoureau, Michel (2001). Blue: The History of a Color. Princeton University Press. ISBN 0-691-09050-5.

Rossotti, Hazel (1983). Colour: Why the World Isn't Grey. Princeton University Press, Princeton, NJ. ISBN 0-691-02386-7.

Simon, Garfield (2000). Mauve: How One Man Invented a Color That Changed the World. Faber and Faber. ISBN 0-393-02005-3.

Wouters, Jan and Noemi Rosario-Chirinos (1992). Dye Analysis of Pre-Columbian Peruvian Textiles with High-Performance Liquid Chromatography and Diode-Array Detection. *Journal of the American Institute for Conservation* (The American Institute for Conservation of Historic Artistic Works), **31(2):** 237-255. doi:10.2307/3179495. JSTOR 3179495.

CHAPTER

13

CLAYS AND ASSOCIATED MINERALS IN CEMENT AND PLASTERS

13.1 THE EVOLUTION OF CEMENT

In the most general sense of the word, a cement is a binder, a substance that sets and hardens independently, and can bind other materials together. The word "cement" traces modern concrete that was made from crushed rock with burnt lime as binder. The volcanic ash and pulverized brick additives that were added to the burnt lime to obtain a hydraulic binder were later referred to as cementum, cimentum and cement. Cement used in construction is characterized as hydraulic cement and non-hydraulic cement. Hydraulic cements harden because of hydration and chemical reactions that occur independently of the mixture's water content, so they can harden even under water or when constantly exposed to wet weather; whereas non-hydraulic cements must be kept dry in order to retain their strength. Example of hydraulic cement is Portland cement and non-hydraulic cement is lime and gypsum plaster. Besides this the most important use of cement is the production of mortar and concrete. The term cement refers to the material used to bind the aggregate materials of concrete. Concrete is a strong building material that is durable in the face of normal environmental effects.

13.2 EARLY USES

It is uncertain where it was first discovered that a combination of hydrated non-hydraulic lime and a pozzolan produces a hydraulic mixture (see also: Pozzolanic reaction), but concrete made from such mixtures was first used by the Ancient Macedonians and three centuries later on a large scale by Roman engineers. They used both natural pozzolans (trass or pumice) and artificial pozzolans (ground brick or pottery) in these concretes. Many excellent examples of structures made from these concretes are still standing, notably the huge

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monolithic dome of the Pantheon in Rome and the massive Baths of Caracalla. The vast system of Roman aqueducts also made extensive use of hydraulic cement. Although any preservation of this knowledge in literary sources from the Middle Ages is unknown, medieval masons and some military engineers maintained an active tradition of using hydraulic cement in structures such as canals, fortresses, harbours and shipbuilding facilities.

13.3 MODERN CEMENT

Modern hydraulic cements began to be developed from the start of the Industrial Revolution (around 1800), driven by three main needs:

- Hydraulic cement render (stucco) for finishing brick buildings in wet climates.
- Hydraulic mortars for masonry construction of harbour works, etc.
- Development of strong concretes.

The most common type of cement used by concrete manufacturers is Portland cement, which is prepared by igniting a mixture of raw materials mainly composed of calcium carbonate or aluminium silicates. Portland cement can be defined as "hydraulic cement produced by pulverizing clinker consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulphate as an interground addition". The phase compositions in Portland cement are denoted as tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF).

Table 13.1: Components of Portland cement

Name of component	*Phase*	*Formula*	*Composition in %*
Tricalcium silicate	(C_3S)	$3CaO\ SiO_2$	49
Dicalcium silicate	(C_2S)	$2CaO\ SiO_2$	25
Tricalcium aluminate	(C_3A)	$3CaO\ Al_2O_3$	12
Tetracalcium aluminoferrite	(C_4AF)	$4CaO\ Al_2O_3\ Fe_2O_3$	9

13.4 CHEMISTRY OF CEMENT

Hydration is the reaction that takes place between cement and water that leads to setting and hardening. All compounds present in Portland cement clinker are anhydrous, but when brought into contact with water, they are all attacked or decomposed, forming hydrated compounds. When the tri- or di-calcium silicates react with water a calcium-silicate-hydrate gel is formed. The chemical reactions that take place during hydration are summarized below:

- **Tricalcium silicate**

$$2(3CaO \cdot SiO_2) + 6HO_2 \longrightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2$$

- **Dicalcium silicate**

  $2(2CaO\cdot SiO_2) + 4H_2O \longrightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + Ca(OH)_2$

- **Tricalcium aluminate**

  $3CaO\cdot Al_2O_3 + 6H_2O \longrightarrow 3CaO\cdot Al_2O_3\cdot 6H_2O$

- **Tetracalcium aluminoferrite**

  $$4CaO\cdot Al_2O_3\cdot Fe_2O_3 + 2Ca(OH)_2 + 10H_2O \longrightarrow 3CaO\cdot Al_2O_3\cdot 6H_2O + 3CaO\cdot Fe_2O_3\cdot 6H_2O$$

13.5 TYPES OF MODERN CEMENT

Masonry cements: These are used for preparing bricklaying mortars and stuccos, and must not be used in concrete. They are usually complex proprietary formulations containing Portland clinker and a number of other ingredients that may include limestone, hydrated lime, air entrainers, retarders, water proofers and colouring agents.

Expansive cements: Expansive cements, in addition, Portland clinker, expansive clinker and are designed to offset the effect of the constituent materials.

White blended cements: It is used to produce white clinker and white supplementary materials such as high-purity metakaolin.

Coloured cements: They are used to produce coloured Portland cement and it is used simultaneously in decorative purpose.

Very finely ground cements: They are made from mixtures with sand or slag. It is very dusty material.

13.6 CEMENT MANUFACTURING

Raw Materials

The main raw materials used in the cement manufacturing process are limestone, sand, shale, clay and iron ore. The main material, limestone, is usually mined on site while the other minor materials may be mined either on site or in nearby quarries. Another source of raw materials is industrial by-products. The use of by-product materials to replace natural raw materials is a key element in achieving sustainable development.

Raw Material Preparation

Mining of limestone requires the use of drilling and blasting techniques. The blasting techniques use the latest technology to ensure that vibration, dust and noise emissions are kept at a minimum. Blasting produces materials in a wide range of sizes from approximately 1.5 metres in diameter to small particles less than a few millimetres. Material is loaded at the blasting face into trucks for transportation to the crushing plant. Through a series of crushers and screens, the limestone is reduced to a size less than 100 mm and stored until required. Depending on size, the minor materials (sand, shale, clay and iron ore) may or may not be crushed before being stored in separate areas until required.

Raw Grinding

In the wet process, each raw material is proportioned to meet a desired chemical composition and fed to a rotating ball mill with water. The raw materials are ground to a size where the majority of the materials are less than 75 microns. Materials exiting the mill are called “slurry” and have flow ability characteristics. This slurry is pumped to blending tanks and homogenized to ensure that the chemical composition of the slurry is correct. Following the homogenization process, the slurry is stored in tanks until required. In the dry process, each raw material is proportioned to meet a desired chemical composition and fed to either a rotating ball mill or vertical roller mill. The raw materials are dried with waste process gases and ground to a size where the majority of the materials are less than 75 microns. The dry materials exiting either type of mill are called “kiln feed”. The kiln feed is pneumatically blended to ensure that the chemical composition of the kiln feed is well homogenized and then stored in silos until required.

Pyroprocessing

Whether the process is wet or dry, the same chemical reactions take place. Basic chemical reactions are: evaporating all moisture, calcining the limestone to produce free calcium oxide, and reacting the calcium oxide with the minor materials (sand, shale, clay and iron). This results in a final black, nodular product known as “clinker” which has the desired hydraulic properties. In the wet process, the slurry is fed to a rotary kiln, which can be from 3.0 m to 5.0 m in diameter and from 120.0 m to 165.0 m in length. The preheater tower and rotary kiln are made of steel and lined with special refractory materials to protect it from the high process temperatures. Process temperatures can reach as high as 1450°C during the clinker making process. Regardless of the process, the rotary kiln is fired with an intense flame, produced by burning coal, coke, oil, gas or waste fuels. Preheater towers can be equipped with firing as well. The rotary kiln discharges the red-hot clinker under the intense flame into a clinker cooler. The clinker cooler recovers heat from the clinker and returns the heat to the pyroprocessing system thus reducing fuel consumption and improving energy efficiency. Clinker leaving the clinker cooler is at a temperature conducive to being handled on standard conveying equipment.

Finish Grinding and Distribution

The black, nodular clinker is stored on site in silos or clinker domes until needed for cement production. Clinker, gypsum and other process additions are ground together in ball mills to form the final cement products. Fineness of the final products, amount of gypsum added, and the amount of process additions added are all varied to develop a desired performance in each of the final cement products. In the dry process, kiln feed is fed to a preheater tower, which can be as high as 150.0 metres. Material from the preheater tower is discharged to a rotary kiln which can have the same diameter as a wet process kiln but the length is much shorter at approximately 45.0 m. Each cement product is stored in an individual bulk silo until needed by the customer. Bulk cement can be distributed by truck, rail, or water depending on the customer's needs. Cement can also be packaged with or without colour addition and distributed by truck or rail.

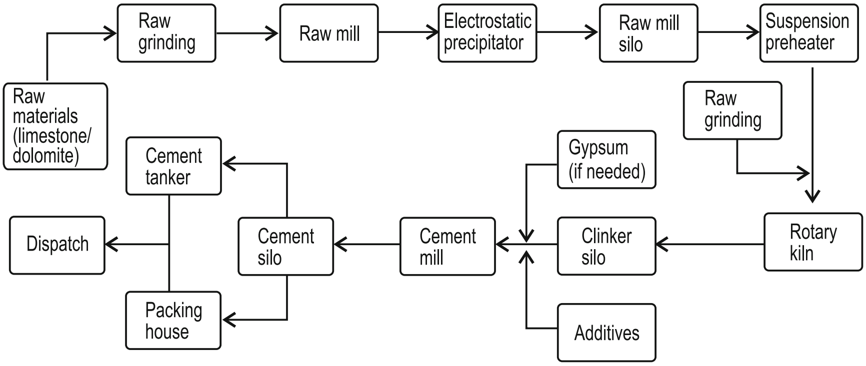

Fig. 13.1: Processing of cement

13.7 USE OF CEMENT

The most important use of cement is the production of mortar and concrete—the bonding of natural or artificial aggregates to form a strong building material that is durable in the face of normal environmental effects. The term cement refers to the material used to bind the aggregate materials of concrete. Concrete is a combination of cement and aggregate.

13.8 PORTLAND CEMENT

Cement is made by heating limestone (calcium carbonate) with small quantities of other materials (such as clay) to 1450°C in a kiln, in a process known as calcination, whereby a molecule of carbon dioxide is liberated from the calcium carbonate to form calcium oxide, or quicklime, which is then blended with the other materials that have been included in the mix. The resulting hard substance, called 'clinker', is then ground with a small amount of gypsum into a powder to make 'Ordinary Portland Cement', the most commonly used type of cement (often referred to as OPC).

Portland cement is a basic ingredient of concrete, mortar and most non-speciality grout. The most common use for Portland cement is in the production of concrete. Concrete is a composite material consisting of aggregate (gravel and sand), cement, and water. As a construction material, concrete can be cast in almost any shape desired, and once hardened, can become a structural (load bearing) element. Portland cement may be grey or white.

13.9 PORTLAND CEMENT BLENDS

Portland cement blends are often available as inter-ground mixtures from cement manufacturers, but similar formulations are often also mixed from the ground components at the concrete mixing plant.

Portland blast-furnace cement: It contains upto 70% ground granulated blast furnace slag, with the rest Portland clinker and a little gypsum. All compositions produce high ultimate strength, but as slag content is increased, early strength is reduced, while sulphate resistance increases and heat evolution diminishes. Used as an economic alternative to Portland sulphate-resisting and low-heat cements.

Portland fly-ash cement: It contains upto 30% fly ash. The fly ash is pozzolanic, so that ultimate strength is maintained. Because fly ash addition allows a lower concrete water content, early strength can also be maintained. Where good quality cheap fly ash is available, this can be an economic alternative to ordinary Portland cement.

Portland pozzolan cement: It includes fly ash cement, since fly ash is a pozzolan, but also includes cements made from other natural or artificial pozzolans. In countries where volcanic ashes are available (e.g. Italy, Chile, Mexico and the Philippines), these cements are often the most common form in use.

Portland silica fume cement: Addition of silica fume can yield exceptionally high strengths, and cements containing 5-20% silica fume are occasionally produced. However, silica fume is more usually added to Portland cement at the concrete mixer.

Masonry cements: These are used for preparing bricklaying mortars and stuccos, and must not be used in concrete. They are usually complex proprietary formulations containing Portland clinker and a number of other ingredients that may include limestone, hydrated lime, air entrainers, retarders, water-proofers and colouring agents. They are formulated to yield workable mortars that allow rapid and consistent masonry work. Subtle variations of masonry cement in the US are plastic cements and stucco cements. These are designed to produce controlled bond with masonry blocks.

Expansive cements: It contains, in addition to Portland clinker, expansive clinkers (usually sulphoaluminate clinkers), and are designed to offset the effects of drying shrinkage that is normally encountered with hydraulic cements. This allows large floor slabs (up to 60 m square) to be prepared without contraction joints.

White blended cements: It may be made using white clinker and white supplementary materials such as high-purity metakaolin.

Coloured cements: These are used for decorative purposes. In some standards, the addition of pigments to produce “coloured Portland cement” is allowed. In other standards (e.g. ASTM), pigments are not allowed constituents of Portland cement, and coloured cements are sold as “blended hydraulic cements”.

Very finely ground cements: These are made from mixtures of cement with sand or with slag or other pozzolan type minerals that are extremely finely ground together. Such cements can have the same physical characteristics as normal cement but with 50% less cement particularly due to their increased surface area for the chemical reaction. Even with intensive grinding they can use upto 50% less energy to fabricate than ordinary Portland cements.

13.10 NON-PORTLAND HYDRAULIC CEMENTS

Pozzolan-lime cements: Mixtures of ground pozzolan and lime are the cements used by the Romans, and can be found in Roman structures still standing (e.g. the Pantheon in Rome). They develop strength slowly, but their ultimate strength can be very high. The hydration products that produce strength are essentially the same as those produced by Portland cement.

Slag-lime cements: Ground granulated blast furnace slag is not hydraulic on its own, but is “activated” by addition of alkalis, most economically using lime. They are similar to pozzolan lime cements in their properties. Only granulated slag (i.e. water-quenched, glassy slag) is effective as a cement component.

Supersulphated cements: These contain about 80% ground granulated blast furnace slag, 15% gypsum or anhydrite and a little Portland clinker or lime as an activator. They produce strength by formation of ettringite, with strength growth similar to a slow Portland cement. They exhibit good resistance to aggressive agents, including sulphate.

Calcium aluminate cements: These are hydraulic cements made primarily from limestone and bauxite. The active ingredients are monocalcium aluminate $CaAl_2O_4$ ($CaO \cdot Al_2O_3$ or CA in Cement chemist notation, CCN) and mayenite $Ca_{12}Al_{14}O_{33}$ ($12\ CaO \cdot 7\ Al_2O_3$, or C12A7 in CCN). Strength forms by hydration to calcium aluminate hydrates. They are well-adapted for use in refractory (high-temperature resistant) concretes, e.g. for furnace linings.

Calcium sulphoaluminate cements: These are made from clinkers that include ye’elimite ($Ca_4(AlO_2)_6SO_4$ or C4A3 in Cement chemist notation) as a primary phase. They are used in expansive cements, in ultra-high early strength cements, and in “low-energy” cements. Hydration produces ettringite, and specialized physical properties (such as expansion or rapid reaction) are obtained by adjustment of the availability of calcium and sulphate ions. Their use as a low-energy alternative to Portland cement has been pioneered in China, where several million tonnes per year are produced. Energy requirements are lower because of the lower kiln temperatures required for reaction, and the lower amount of limestone (which must be endothermically decarbonated) in the mix. In addition, the lower limestone content and lower fuel consumption leads to a CO_2 emission around half that associated with Portland clinker. However, SO_2 emissions are usually significantly higher.

13.11 THE SETTING OF CEMENT

Cement sets when mixed with water by way of a complex series of hydration chemical reactions still only partly understood. The different constituents slowly hydrate and crystallise while the interlocking of their crystals gives to cement its strength. After the initial setting, immersion in warm water will speed up setting. In Portland cement, gypsum is added as a compound preventing cement flash setting. The time it takes for cement to set varies and can take anywhere from twenty minutes for initial set, to twenty-four hours, or more, for final set.

13.12 TYPES OF PLASTERS

Plaster is an important building material used for various aspects such as coating walls, ceilings etc. Plaster starts as a dry powder similar to cement and like those materials it is mixed with water to form a paste which liberates heat and then hardens. Unlike cement, plaster remains quite soft after setting, and can be easily manipulated with metal tools. These characteristics make plaster suitable for a finishing, rather than a load-bearing material. In medical science it plays an important role as a binding material to do plasters because of its semi-liquid nature with presence of water. The term Plaster of Paris can refer to gypsum plaster; besides this another two types of plasters are well known: lime plaster and cement plaster.

Gypsum plaster: It is produced by mixing water with calcium sulphate hemihydrate, with the help of heat of about 300°F (150°C). When the dry plaster powder is mixed with water, it re-forms into gypsum. If plaster or gypsum is heated above 200°C, anhydrite is formed, which will also re-form as gypsum if mixed with water.

Gypsum plaster is often being used to simulate the appearance of surfaces of wood, stone, or metal.

Lime plaster: Lime plaster is a mixture of calcium hydroxide and sand. With the presence of carbon dioxide, calcium hydroxide change into calcium carbonate (limestone). To make lime plaster, limestone is heated to produce quicklime. Thus calcium carbonate change to calcium oxide, then water is added to produce slaked lime (calcium hydroxide). Additional water is added to form a paste and stored in air-tight containers as if it exposed to the atmosphere, the calcium hydroxide turns back into calcium carbonate.

Cement plaster: It is a mixture of suitable plaster, sand, Portland cement and water which is normally applied to masonry interiors and exteriors to achieve a smooth surface. Walls constructed with stock bricks are normally plastered while face brick walls are not plastered. Various cement-based plasters are also used as proprietary spray fireproofing products. These usually use vermiculite as lightweight aggregate. Heavy versions of such plasters are also in use for exterior fireproofing, to protect LPG vessels, pipe bridges and vessel skirts.

13.13 USES OF PLASTER

In Architecture

Plaster is used to create complex detailing for use in room interiors. These may be geometric (simulating wood or stone) or naturalistic (simulating leaves, vines and flowers). These are also often used to simulate wood or stone detailing found in more substantial buildings.

In Art

In the past the famous painters used thin layer of wet plaster to paint on it, known as intonaco. The pigments sink into this layer so that the plaster itself becomes the medium holding them, which accounts for the excellent durability.

Plaster may be cast directly into a damp clay mold. In creating this piece, molds or waste molds would be made of plaster. Some product of plaster when fired in a kiln become terra cotta building decorations, or these may be used to create cast concrete sculptures. If a plaster positive was desired this would be constructed or cast to form a durable image artwork. As a model for stonecutters this would be sufficient. If intended for producing a bronze casting the plaster positive could be further worked to produce smooth surfaces. An advantage of this plaster image is that it is relatively cheap; should a patron approve of the durable image and be willing to bear further expense, subsequent molds could be made for the creation of a wax image to be used in wax casting, a far more expensive process. In lieu of producing a bronze image suitable for outdoor use the plaster image may be painted to resemble a metal image; such sculptures are suitable only for presentation in a weather-protected environment. Plaster expands while hardening, and then contracts slightly just before hardening completely. This makes plaster excellent for use in molds, and it is often used as an artistic material for casting.

In Medicine

Plaster is widely used as a support for broken bones; a bandage impregnated with plaster is moistened and then wrapped around the damaged limb, setting into a close-fitting yet easily removed tube, known as an orthopaedic cast. Plaster is also used within radiotherapy when making immobilization cast for patients. Plaster bandages are used when constructing an impression of the patients head and neck, and liquid plaster is used to fill the impression and produce a plaster bust. Perspex is then vacuum formed over this bust creating an immobilization shell.

In Fire Protection

Plasters have been in use in passive fire protection, as fireproofing products, for many decades. The finished plaster releases water vapour when exposed to flame, acting to slow the spread of the fire, for as much as an hour or two depending on thickness. It also provides some insulation to retard heat flow into structural steel elements, which would otherwise lose their strength and collapse in a fire. Early versions of these plasters have used asbestos fibres, which have by now been outlawed in industrialized nations and have caused significant removal and re-coating work.

More modern plasters fall into the following categories:

- Fibrous (including mineral wool and glass fibre).
- Cement mixtures either with mineral wool or with vermiculite.
- Gypsum plasters, leavened with polystyrene beads, as well as chemical expansion agents to decrease the density of the finished product.

One differentiates between interior and exterior fireproofing. Interior products are typically less substantial, with lower densities and lower cost. Exterior products have to withstand more extreme fire and other environmental conditions. Exterior products are also more likely to be attractively tooled, whereas their interior cousins are usually merely sprayed in place.

13.14 SAFETY MEASURES IN PLASTERING

The chemical reaction that occurs when plaster is mixed with water is exothermic in nature and can therefore cause severe burns. Some variations of plaster that contains powdered silica or asbestos may present health hazards if inhaled. Asbestos is a known irritant; when inhaled in powder form can cause cancer, especially in people who smoke, and inhalation can also cause asbestosis. Inhaled silica can cause silicosis and (in very rare cases) can encourage the development of cancer. Persons working regularly with plaster containing these additives should take precautions to avoid inhaling powdered plaster, cured or uncured. Asbestos is rarely used in modern plaster formulations because of its carcinogenic effects.

QUESTIONS

1. Give the name of components with formula?
2. What is the role of modern cement?
3. Give a distinct idea on manufacture of cement with a clear flow chart diagram.
4. What are the types of Portland cement?
5. What is the setting of cement?
6. What are the types of plaster with its uses?

FURTHER READING

Berkes, Howard (2011). EPA Regulations Give Kilns Permission To Pollute: NPR. NPR.org. Retrieved 2011-11-17.

Bye, G.C. (1999). Portland Cement (2nd Ed.). ISBN 0-7277-2766-4.

Chandak, Shobhit (2011). Report on cement industry in India.

Deer, Howie and Zussman (1992). An Introduction to the Rock Forming Minerals (2nd Edition). Pearson Education Limited, England.

Heracles to Alexander The Great: Treasures from the Royal Capital of Macedon—A Hellenic Kingdom in the Age of Democracy. Ashmolean Museum of Art and Archaeology. University of Oxford.

Jha, Alok (2008). Revealed: The cement that eats carbon dioxide. *The Guardian* (London). Retrieved 2010-04-28.

Kosmatka, S.H. and Panarese, W.C. (1988). Design and Control of Concrete Mixtures. Portland Cement Association, Skokie, IL, USA.

Li Yong Yan (2004). China's way forward paved in cement. *Asia Times*.

Mahasenan, Natesan, Steve Smith, Kenneth Humphreys and Kaya, Y. (2003). The Cement Industry and Global Climate Change: Current and Potential Future Cement Industry CO_2 Emissions. Greenhouse Gas Control Technologies – 6th International Conference. Oxford: Pergamon.

Mukerji, Chandra (2009). Impossible engineering: Technology and territoriality on the Canal du Midi (Illustrated edition). Princeton University Press. ISBN 978-0-691-14032-2.

Pyatt, Jamie (2011). Mums horror cement burns. *The Sun* (London). Retrieved 2011-02-15.

Scalenghe, R., Malucelli, F., Ungaro, F., Perazzone, L., Filippi, N. and Edwards, A.C. (2011). Influence of 150 years of land use on anthropogenic and natural carbon stocks in Emilia-Romagna Region (Italy). *Environmental Science & Technology*, **45(12):** 5112–5117. doi:10.1021/es1039437.

Schmidt, V.E., Somerset, J.H. and Porter, R.E. (1973). Mechanical Properties of Orthopeadic Plaster Bandages. *Journal of Biomechanics* (Elsevier), **6:** 173-185.

Sismondo, Sergio (2009). An Introduction to Science and Technology Studies (2nd edition, illustrated). John Wiley and Sons.

CHAPTER

14

CLAY AND ASSOCIATED MINERALS IN BATTERY INDUSTRY

14.1 MANGANESE MINERAL

Manganese is found in combination with iron and in many minerals in nature. Some manganese minerals are pyrolusite (MnO_2), braunite ($3Mn_2O_3.MnSiO_3$), rhodochrosite ($MnCO_3$), rhodonite ($MnSiO_3$), manganite ($Mn_2O_3.H_2O$) etc. Manganese ore is produced in huge quantity in India. The total reservoir of manganese ore deposits in India as per IBM report, are placed at ground 154 million tonnes (with proved 18 million tonnes and probably 38 million tonnes and possible 98 million tonnes).

World War II-era nickel made from a 56% copper, 35% silver, 9% manganese alloy. Methyl cyclopentadienyl manganese tricarbonyl is used as an additive in unleaded gasoline to boost octane rating and reduce engine knocking. Manganese oxide (manganese dioxide, MnO_2) is used as a reagent in organic chemistry for the oxidation of benzylic alcohols (i.e. adjacent to an aromatic ring). MnO_2 is also used in the manufacture of oxygen and chlorine, and in drying black paints. In some preparations, it is a brown pigment that can be used to make paint. The metal is very occasionally used in coins; until 2000, the only United States coin to use manganese was the “wartime” nickel during 1942-1945. An alloy of 75% copper and 25% nickel was traditionally used for the production of nickel coins. However, because of shortage of nickel metal during the war, it was substituted by more available silver and manganese, thus resulting in an alloy of 56% copper, 35% silver and 9% manganese. Manganese compounds have been used as pigments and for the colouring of ceramics and glass. In the glass industry, manganese compounds are also used. Manganese reacts with iron to induce a strong green colour in glass by forming

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less-coloured iron and slightly pink manganese, compensating for the residual colour of the iron. Larger amounts of manganese are used to produce pink coloured glass.

Manganese ore is also used in the making of batteries which have 80-86 per cent of manganese oxide, while the content of iron and aluminium should not exceed 10 per cent. Chemistry of primary and rechargeable battery is given in Tables 14.2 and 14.3. Nowadays, of course, low-grade manganese ores are used after purification in the making of batteries.

Table 14.1: Mineral constituents of battery

Mineral constituents	*Battery grade (per cent)*
MnO_2	80-84
Total iron-content (including magnetic iron)	Less than 2.5
Fe_2O_3+Al_2O_3	Max. 10
Cu	Less than 0.3
Acid soluble	Max. 10

Manganese mineral deposits are observed mainly as five types from aspect of origin. These are hydrothermal deposit, sedimentary deposit, residual deposit, metasomatic replacement deposit and metamorphic deposit. Manganese ore is principally used in the manufacture of ferro-manganese and steel. Moreover, it is also used in small quantities in paint and glass. In dry cell batteries *manganese dioxide* is used. Manganese ore is basically mined in Madhya Pradesh, Andhra Pradesh, Orissa, Maharashtra and Karnataka. Though the manganese ore occurred at different places in Indian Plateau, it is found in large quantities in Bhandara, Nagpur and Balaghat districts. These places are situated close to each other in the central and western regions of the country. Of the total manganese ore reserves in the country, Balaghat-Nagpur-Bhandara manganese belt accounts for a hugh portion. Orissa is considered as the leading producer of manganese ore in the country. In these states, manganese ore is mainly mined in Keonjhar and Sundargarh districts. These two districts are leading manganese ore producers with huge tonnes of production. After Orissa, Karnataka is second leading producer of manganese ore in the country. Here, manganese ore is mainly mined in Bellary, Shimoga and North Kanara districts. Further, Nagpur and Bhandara districts of Maharashtra, and Balaghat district of Madhya Pradesh are other important places where manganese ore is mined. Managese minerals are also produced as manganese nodules lie on the seabed sediment, often partly or completely buried. They vary greatly in abundance, in some cases touching one another and covering more than 70% of the sea floor.

Fig. 14.1: Manganese minerals.

14.2 DEVELOPMENT OF BATTERIES

Battery is a collection of multiple electrochemical cells, but in popular usage battery often refers to a single cell. It converts stored chemical energy into electrical energy. The first electrochemical cell was developed by the Italian physicist Alessandro Volta in 1792, and in 1800 he invented the first battery, a "pile" of many cells in series. Although early batteries were of great value for experimental purposes, in practice their voltages fluctuated and they could not provide a large current for a sustained period. Later, starting with the Daniell cell in 1836, batteries provided more reliable currents and were adopted by industry for use in stationary devices. These wet cells used liquid electrolytes, which were prone to leakage and spillage if not handled correctly. Many used glass jars to hold their components, which made them fragile. These characteristics made wet cells unsuitable for portable appliances. Near the end of the nineteenth century, the invention of dry cell batteries, which replaced the liquid electrolyte with a paste, made portable electrical devices practical. Since then, batteries have gained popularity as they became portable and useful for a variety of purposes.

14.3 TWO TYPES OF BATTERIES

Primary Batteries

These batteries irreversibly transform chemical energy to electrical energy. When the initial supply of reactants is exhausted, energy cannot be readily restored to the battery by electrical means, so these batteries are designed to be used once and discarded. Thus these are also called disposable batteries. Common types of disposable batteries include zinc-carbon batteries and alkaline batteries. In general, these have higher energy densities than rechargeable batteries.

Secondary Batteries

These batteries are designed to be recharged and used multiple times. That is, they can have their chemical reactions reversed by supplying electrical energy to the cell, restoring their original composition. Thus these are also called rechargeable batteries. Cells of this type include nickel-cadmium (NiCd), nickel-zinc (NiZn), and lithium-ion (Li-ion) cells.

14.4 PRINCIPLE OF OPERATION

A battery is a device that converts chemical energy directly to electrical energy. It consists of a number of voltaic cells; each voltaic cell consists of two half-cells connected in series by a conductive electrolyte containing anions and cations. One half-cell is anode and another is cathode. In the redox reaction, cations are reduced (electrons are added) at the cathode, while anions are oxidized (electrons are removed) at the anode. The electrodes do not touch each other but are electrically connected by the electrolyte. Each half-cell has an electromotive force (or emf), determined by its ability to drive electric current from the interior to the exterior of the cell. The net emf of the cell is the difference between the emfs of its half-cells, as first recognized by Volta. The electrical driving force of a cell is known as the terminal voltage, measured in volts. The terminal voltage of a cell that is neither charging nor discharging is called the open-circuit voltage. An ideal cell has negligible internal resistance, so it would maintain a constant terminal voltage until exhausted, then dropping to zero. If such a cell maintained 1.5 volts and stored a charge of one coulomb then on complete discharge it would perform 1.5 joule of work. So, the voltage developed depends on the energy release of the chemical reactions of its electrodes and electrolyte.

14.5 BATTERY CELL TYPES

There are many general types of electrochemical cells, the variation includes galvanic cells, electrolytic cells, fuel cells and flow cells.

Wet Cell

A wet cell battery has a liquid electrolyte. It is also called as flooded cell, since the liquid covers all internal parts. Wet cells were a precursor to dry cells and are commonly used as a tool for electrochemistry. A particular type of wet cell known as a concentration cell is important in understanding corrosion. Wet cells may be primary or secondary cells. Some other primary wet cells are the Leclanche cell, Grove cell, Bunsen cell, chromic acid cell, etc. Wet cells are used in automobile batteries and telecommunication.

Dry Cell

A dry cell has the electrolyte immobilized as a paste, with only enough moisture in the paste to allow current to flow. As opposed to a wet cell, the battery can be operated in any random position, and will not spill its electrolyte if inverted.

While a dry cell's electrolyte is not truly completely free of moisture and must contain some moisture to function, it has the advantage of containing no sloshing liquid and consequently making it highly suitable for small portable electric devices.

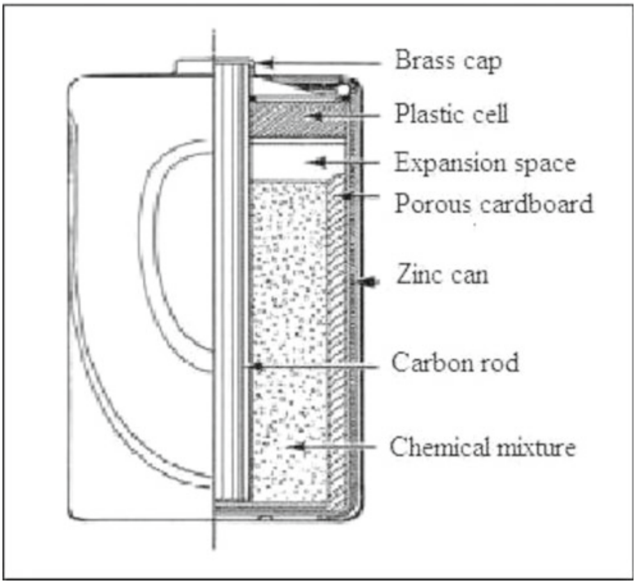

Fig. 14.2: Schematic diagram of a dry cell.

A common dry cell battery is the zinc-carbon battery, using dry Leclanché cell, with a nominal voltage of 1.5 volts.

A standard dry cell is made with a zinc anode (negative pole), in the form of a cylindrical pot, with a carbon cathode (positive pole) in the form of a central rod. The electrolyte is ammonium chloride in the form of a paste. Ammonium chloride and manganese dioxide are present in the remaining space between the electrolyte and carbon cathode. In some modern types of 'high-power' batteries, the ammonium chloride has been replaced by zinc chloride.

14.6 MOLTEN SALT BATTERY

A molten salt battery is a primary or secondary battery that uses a molten salt as its electrolyte. Molten salt batteries are a class of primary cell and secondary cell high-temperature electric battery. These types of batteries are used where high energy density and high power density are required. Their energy density and power density give them potential for use in electric vehicles.

14.7 RESERVE BATTERY

A reserve battery can be stored for a long period of time and is activated when its internal parts are assembled. For example, a battery for an electronic fuse might be activated by the impact of firing a gun, breaking a capsule of electrolyte to activate the battery and power the fuse's circuits. In this condition, chemical deterioration or self-discharge is essentially eliminated, and the battery is capable of long-term storage. Usually the electrolyte is the component that is isolated. The reserve battery design is used to meet extremely long or environmentally severe storage requirements that cannot be met with an "active" battery designed for the same performance characteristics. These batteries are used, for example, to deliver high power for relatively short periods of time, in missiles and other weapon systems.

14.8 FASTEST CHARGING AND LARGEST BATTERIES

Lithium iron phosphate ($LiFePO_4$) batteries were the fastest-charging and discharging batteries (supercapacitors, in some ways comparable to batteries, charge faster). The world's largest battery, composed of Ni-Cd cells, is in Fairbanks, Alaska. Sodium-sulphur batteries were being used to store wind power. Lithium-sulphur batteries have been used on the longest and highest solar-powered flight. The speed of recharging of lithium-ion batteries can be increased by manufacturing changes.

14.9 BATTERY CAPACITY AND DISCHARGING

A battery's cell performance may vary over load cycle, over charge cycle, and over lifetime due to many factors including internal chemistry and temperature.

A battery's *capacity* is the amount of electric charge which the battery can store. If there is more electrolyte and electrode material in the cell, capacity of the cell will be greater. A small cell has less capacity than a larger cell with the same chemistry. Because of the chemical reactions within the cells, the capacity of a battery depends on the discharge conditions such as the magnitude of the current. If a battery is discharged at a relatively high rate, the available capacity will be lower than expected.

The relationship between current, discharge time, and capacity for a lead acid battery is approximated (over a certain range of current values) by Peukert's law:

$$t = \frac{Q_P}{I^k}$$

where Q_P is the capacity when discharged at a rate of 1 amp., I is the current drawn from battery, t is the amount of time (in hours) that a battery can sustain and k is a constant around 1.3.

In practical batteries, internal energy losses and limited rate of diffusion of ions through the electrolyte cause the efficiency of a battery to vary at different discharge rates. When discharging at low rate, the battery's energy is delivered more efficiently than at higher discharge rates, but if the rate is too low, it will self-discharge during the long time of operation, again lowering its efficiency.

14.10 BATTERY CHEMISTRY

A battery is a package of one or more galvanic cells used for the production and storage of electric energy by chemical means. A galvanic cell consists of at least two half cells, a reduction cell and an oxidation cell. Chemical reactions in the two half cells provide the energy for the galvanic cell operations. Each half cell consists of an electrode and an electrolyte solution. Usually the solution contains ions derived from the electrode by oxidation or reduction reaction. It can be demonstrated through a galvanic cell which is also called a voltaic cell. The spontaneous reactions in it provide the electric energy or current. Two half cells can be put together to form an electrolytic cell, which is used for electrolysis. In this case, electric energy is used to force non-spontaneous chemical reactions. Oxidation and reduction both play an important role. Oxidation indicates loss of electrons and gain of electrons indicated by reduction. Oxidation and reduction reactions cannot be carried out separately. They have to appear together in a chemical reaction. Thus oxidation and reduction reactions are often called redox reactions. In terms of redox reactions, a reducing agent and an oxidizing agent form a redox. An oxidant is an oxidizing reagent, and a reductant is a reducing agent.

Table 14.2: Chemistry of primary battery

Chemistry	*Cell voltage*	*Specific energy [MJ/kg]*	*Comments*
Zinc-carbon	1.5	0.13	Inexpensive
Zinc-chloride	1.5		Inexpensive
Lithium (lithium-manganese dioxide) $LiMnO_2$	3.0	0.83-1.01	Expensive only used in high-drain devices
Nickel oxyhydroxide	1.7		Good for high drain uses
Silver-oxide	1.55	0.47	Very expensive only used commercially in 'button' cells
Zinc-air	1.35-1.65	1.59	Mostly used in hearing aids
Alkaline	1.5	0.4-0.59	Good for high and low drain uses

Table 14.3: Chemistry of rechargeable battery

Chemistry	*Cell voltage*	*Specific energy [MJ/kg]*	*Comments*
NiCd	1.2	0.14	Inexpensive, used in higher drain devices
Lead-acid	2.1	0.14	Moderately expensive, used in automobile batteries
NiMH	1.2	0.36	Moderately inexpensive, used in some cars
Lithium ion	3.6	0.46	Very expensive, used in laptop computers, moderate to high-end digital cameras and camcorders, and cellphones

14.11 HOME-MADE CELLS

Almost any moist object that has enough ions to be electrically conductive can serve as the electrolyte for a cell. It is possible to insert two electrodes made of different metals into a lemon, potato, etc. and generate small amounts of electricity. Home-made cells of this kind are of no real practical use, because they produce far less current—and cost far more per unit of energy generated—than commercial cells.

Lead acid cells can easily be manufactured at home, but a tedious charge/discharge cycle is needed to 'form' the plates. This is a process in which lead sulfate forms on the plates, and during charge is converted to lead dioxide (positive plate) and pure lead (negative plate). Repeating this process increases the current that cell can deliver.

- Aluminium-air batteries can also be produced with high-purity aluminium.
- Aluminium foil batteries will produce some electricity, but they are not very efficient, in part because a significant amount of hydrogen gas is produced.

14.12 HAZARDS

Explosion

A battery explosion is caused by the malfunction of a battery, such as attempting to recharge a primary (non-rechargeable) battery. Explosions are most likely to occur in car batteries when a short circuit generates very large currents. In addition, car batteries liberate hydrogen when they are overcharged because of electrolysis of the water in the electrolyte. When a battery is recharged at an excessive rate, an explosive gas mixture of hydrogen and oxygen may be produced faster than it can escape from within the walls of the battery, leading to pressure build-up and the possibility of bursting of the battery case. In extreme cases, the battery acid may spray violently from the casing of the battery and cause injury.

Leakage

Many battery chemicals are corrosive, poisonous, or both. If leakage occurs, either spontaneously or through accident, the chemicals released may be dangerous.

Fig. 14.3: Leaked alkaline battery.

14.13 BATTERY LIFETIME

Primary batteries

Even if never taken out of the original package, primary batteries can lose 8 to 20 per cent of their original charge every year at a temperature of about 20°–30°C. This is known as the "self discharge" rate and is due to side chemical reactions, which occur within the cell even if no load is applied to it. The rate of the side reactions is reduced if the batteries are stored at low temperature, although some batteries can be damaged by freezing because high or low temperatures may reduce battery performance.

Secondary batteries

Storage life of secondary batteries is limited by chemical reactions (side reactions) that occur between the battery parts and the electrolyte. Due to this reaction internal parts may corrode and fail, or the active materials may be slowly converted to inactive forms and may be lost due to physical changes of volume; this may limit the life of the battery.

In old chemistry rechargeable batteries self-discharge more rapidly occurred than disposable alkaline batteries, especially nickel-based batteries. However,

Fig. 14.4: Photograph of a dry cell baterry.

newer low self-discharge nickel metal hydride (NiMH) batteries designs have reduced the self-discharge rate to a relatively low level. Most nickel-based batteries are partially discharged when purchased, and must be charged before first use. Newer NiMH batteries are ready to be used when purchased, and have only 15% discharge in a year. Rechargeable batteries have their energy content restored by charging. Low-capacity NiMH batteries can be charged for about 1000 cycles, whereas high-capacity NiMH batteries can be charged for about 500 cycles

Automotive lead-acid rechargeable batteries have a much harder life. The main benefit of the lead-acid battery is its low cost; the main drawbacks are its large size and weight for a given capacity and voltage. Lead-acid batteries should never be discharged to below 20% of their full capacity, because internal resistance will cause heat and damage when they are recharged.

Extending Battery Life

Battery life can be extended by storing the batteries at a low temperature, as in a refrigerator or freezer, which slows the chemical reactions in the battery. Such storage can extend the life of alkaline batteries by about 5%, while the charge of rechargeable batteries can be extended from a few days up to several months.

Prolonging Life in Multiple Cells through Cell Balancing

Battery pack cells are balanced when all the cells in the battery pack meet two conditions:

1. If all cells have the same State of Charge (SOC) and same capacity, they are balanced. In this case, the Open Circuit Voltage (OCV) is a good measure

of the SOC. In an out of balance pack, all cells can be differentially charged to full capacity.

2. If the cells have different capacities but same State of Charge (SOC), they are also considered balanced when the SOC is the same. But, since SOC is a relative measure, the absolute amount of capacity for each cell is different. To keep the cells with different capacities at the same SOC, cell balancing must provide differential amounts of current to cells.

14.14 ENVIRONMENTAL CONCERNS

The widespread use of batteries has created many environmental concerns, such as toxic metal pollution. Battery manufacture consumes resources and often involves chemical hazards. Used batteries also contribute to electronic waste. Some areas now have battery recycling services available to recover some of the materials from used batteries. Recycling or proper disposal prevents dangerous elements (such as lead, mercury and cadmium) found in some types of batteries from entering the environment. In the United States, the Mercury Containing and Rechargeable Battery Management Act of 1996 banned the sale of mercury-containing batteries, enacted uniform labeling requirements for rechargeable batteries, and required that rechargeable batteries be easily removable.

QUESTIONS

1. What are the mineral constituents of battery?
2. What is the role of manganese dioxide in formation of battery?
3. Describe the following items with description:
   Molten salt battery, Reserve battery, Fastest charging, largest and lightest batteries, Battery capacity and discharging.
4. What is dry cell and wet cell?
5. What is chemistry of primary battery and rechargeable battery?
6. Give an idea about the type of hazards made by battery?

FURTHER READING

Amos, J. (2008). Solar plane makes record flight. BBC News.

Bellis, Mary (2008). Biography of Alessandro Volta – Stored Electricity and the First Battery.

Biello, D. (2008). Storing the Breeze: New Battery Might Make Wind Power More Reliable. *Scientific American* (December 22, 2008).

Conway, E. (2008). World's biggest battery switched on in Alaska. *Telegraph.co.ukCorder* (2 September 2008).

Dingrando, Laurel et al. (2007). Chemistry: Matter and Change. McGraw-Hill. New York: Glencoe. ISBN 978-0-07-877237-5.

Ellis, Mary (2008). Biography of Alessandro Volta – Stored Electricity and the First Battery.

Fink, Donald G. and Wayne Beaty, H. (1978). Standard Handbook for Electrical Engineers (Eleventh Edition). McGraw-Hill, New York. ISBN 0-07-020974-X..

Gregory, W. (2008). Using an Unconventional History of the Battery to Engage Students and Explore the Importance of Evidence (PDF). *Virginia Journal of Science Education*, **1(1)**.

Kang, B. and Ceder, G. (2009). Battery materials for ultrafast charging and discharging. *Nature*, **458:** 190-193. 1:00-6:50 (audio).

Knight, Randall D. (2004). Physics for Scientists and Engineers: A Strategic Approach. Pearson Education, San Francisco. ISBN 0-8053-8960-1.

Linden, David and Reddy, Thomas B. (2001). Handbook of Batteries. McGraw-Hill, New York. ISBN 0-07-135978-8.

Rich, Vincent (1994). The International Lead Trade. Woodhead, Cambridge.

Saslow, Wayne M. (2002). Electricity, Magnetism, and Light. Thomson Learning, Toronto. ISBN 0-12-619455-6.

CHAPTER

15

INSULATORS USING CLAYS

15.1 INTRODUCTION

A true insulator is a material that does not respond to an electric field and completely resists the flow of electric charge. However, perfect insulators do not exist. Therefore, dielectric materials with high dielectric constants are considered insulators. In insulating materials valence electrons are tightly bonded to their atoms. These materials are used in electrical equipment as insulators or insulation. Their function is to support or separate electrical conductors without allowing current through themselves. Some materials such as glass, paper or Teflon are very good electrical insulators. Even though they may have lower bulk resistivity, a much larger class of materials are still "good enough" to insulate electrical wiring and cables. Examples include rubber-like polymers and most plastics. Such materials can serve as practical and safe insulators for low to moderate voltages. Mainly insulator is used in two forms: processed and unprocessed. Unprocessed insulator is required as building materials to make mud-hut due to having thermal insulation property and processed insulator having property of electrical insulation such as ceramics, is used in electrical purpose.

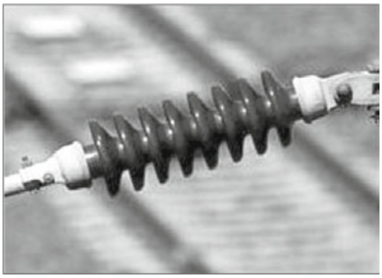

Fig. 15.1: Ceramic insulator at railways.

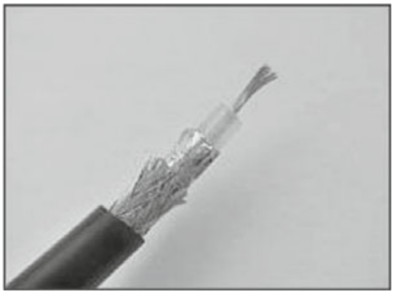

Fig. 15.2: Coaxial cable with dielectric insulator.

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15.2 MATERIAL

Insulators used for high-voltage power transmission are made from glass, porcelain or composite polymer materials. Porcelain insulators are made from clay, quartz or alumina and feldspar, and are covered with a smooth glaze to shed water. Insulators made from porcelain rich in alumina are used where high mechanical strength is a criterion. Porcelain has a dielectric strength of about 4–10 kV/mm. Glass has a higher dielectric strength, but it attracts condensation and the thick irregular shapes needed for insulators are difficult to cast without internal strains. Some insulator manufacturers stopped making glass insulators in the late 1960s, switching to ceramic materials. Recently, some electric utilities have begun converting to polymer composite materials for some types of insulators. These are typically composed of a central rod made of fibre reinforced plastic and an outer weathered made of silicone rubber or EPDM. Composite insulators are less costly, lighter in weight, and have excellent hydrophobic capability. This combination makes them ideal for service in polluted areas.

15.3 ELECTRICAL INSULATION

The most important insulation material is air. A variety of solid, liquid and gaseous insulators are also used in electrical apparatus. In smaller transformers, generators and electric motors, insulation on the wire coils consists of upto four thin layers of polymer varnish film. Film insulated magnet wire permits a manufacturer to obtain the maximum number of turns within the available space. Windings that use thicker conductors are often wrapped with supplemental fibreglass insulating tape. Windings may also be impregnated with insulating varnishes to prevent electrical corona and reduce magnetically induced wire vibration. Large power transformer windings are still mostly insulated with paper, wood, varnish and mineral oil. Although these materials have been used for more than 100 years, they still provide a good balance of economy and adequate performance. Busbars and circuit breakers in switchgear may be insulated with glass-reinforced plastic insulation, treated to have low flame spread and to prevent tracking of current across the material.

In older apparatus made up to the early 1970s, boards made of compressed asbestos may be found. While this is an adequate insulator at power frequencies, handling or repairs to asbestos material will release dangerous fibres into the air and must be carried out with caution. Wire insulated with felted asbestos was used in high-temperature and rugged applications from the 1920s. Wire of this type was sold by General Electric under the trade name “Deltabeston.”

Live-front switchboards upto the early part of the 20th century were made of slate or marble. Some high voltage equipment is designed to operate within a high pressure insulating gas such as sulphur hexafluoride. Insulation materials that perform well at power and low frequencies may be unsatisfactory at radio frequency, due to heating from excessive dielectric dissipation. Electrical wires may be insulated with polyethylene, crosslinked polyethylene etc.

Table 15.1: Solid dielectric for electric insulation

Inorganic		Ceramics (porcelain, alumina, %) Glass, quartz Cements and minerals as mica
Organic	Thermoplastic	Rubber (natural, butyl, silicone) Polyamide (nylon) Polyester (mylar) Polypropylene (PP) Polystyrene (PS) Polyvinyl chloride (PVC) Polymethylmetachrylate (PMMA) Polycarbonate (PC) Polytetrafluoroethylene (PTFE)
	Thermosetting	Polyethylene (PE, LDPE, MDPE, HDPE, XLPE) Ethylene-Propylene (EPR) Polyimide Polyetheretherketone (PEEK) Epoxy, phenolic, silicon, polyester resins
Composites		Kevlar Carbon Fibre glass Mica

Table 15.2: Relative permeability of various materials

Material	*Relative permittivity*
Air	1
Polyester	4
Epoxy	3
Fibre glass	6
Nylon (polyamide)	5
Polymide	4
Polyethylene	2
PVC	3
Transformer oil	2
Mica	5
Butyl rubber	3
Water	80
Alumina	9
Barium titanate	1500

When the electric field is high enough a dielectric may suddenly lose its property of non-conduction, permanently or temporarily, showing an electrical breakdown.

It consists in the abrupt rise of electrical current under the effect of an electric field. Its causes depend on the medium, the geometry and the type and amplitude of the electric field.

- ➔ Medium
  - Solid
  - Liquid
  - Gas
  - Vacuum
- ➔ Geometry
- ➔ Distribution (electric field)
- ➔ Type (dc, ac, impulse, frequency %)
- ➔ Voltage

Table 15.3: The analogy between conductor dielectric voltage and water channel pipe wall pressure

Conductor dielectric voltage	*Water channel pipe wall pressure*
Dielectric breakdown:	*Mechanical failure:*
Happens above certain.	Happens above certain
Difference of voltage between inside and outside the dielectric.	Difference of pressure between inside and outside the pipe wall.
In reality it is the electric field which counts.	In reality it is the mechanical stress which counts.

15.4 THERMAL INSULATION

Thermal insulation is the reduction of heat transfer between objects in thermal contact or in range of radioactive influence. Heat transfer is the transfer of thermal energy between objects of differing temperature. The means to stem heat flow may be especially engineered methods or processes, as well as suitable static objects and materials. Heat flow is an inevitable consequence of contact between objects of differing temperature. Thermal insulation provides a means to maintain a gradient of temperature, by providing a region of insulation in which heat flow is reduced or thermal radiation is reflected rather than absorbed. In building construction, insulating materials are assigned a quantitative measure of the insulating capability, called the R-value. In thermal engineering of insulating systems for ovens, reactors and furnaces, thermal conductivity (K), product density and specific heat (C) are the key product characteristics, which influence insulating efficiency, such as acolodet insulating. Low thermal conductivity (K) is analogous to high insulating capability (R).

15.5 BUILDING INSULATION

Building insulation refers broadly to any object in a building used as insulation for any purpose. While the majority of insulation in buildings is for thermal purposes, the term also applies to acoustic insulation, fire insulation, and impact insulation (e.g. for vibrations caused by industrial applications). Often an insulation material will be chosen for its ability to perform several of these functions at once. Thermal insulation in buildings is an important factor to achieve thermal comfort for its occupants. Insulation reduces unwanted heat loss or gain and can decrease the energy demands of heating and cooling systems. It does not necessarily deal with issues of adequate ventilation and may or may not affect the level of sound insulation. In a narrow sense insulation can just refer to the insulation materials employed to slow heat loss, such as: cellulose, glass wool, rock wool, polystyrene, urethane foam, vermiculite, perlite, wood fibre, plant fibre (canabis, flax, cotton, cork, etc.), plant straw, animal fibre (sheep's wool), cement, and earth or soil, but it can also involve a range of designs and techniques to address the main modes of heat transfer — conduction, radiation and convection materials.

15.6 BREAKDOWN

By the process influence, some physical and chemical factors destroy insulator, known as insulator breakdown. Insulators suffer from the phenomenon of electrical breakdown. When the electric field applied across an insulating substance exceeds in any location the threshold breakdown field for that substance, which is proportional to the band gap energy, the insulator suddenly turns into a resistor, sometimes with catastrophic results. During electrical breakdown, any free charge carrier being accelerated by the strong e-field will have enough velocity to knock electrons from (ionize) any atom it strikes. These freed electrons and ions are in turn accelerated and strike other atoms, creating more charge carriers, in a chain reaction. Rapidly the insulator becomes filled with mobile carriers, and its resistance drops to a low level. In air, "corona discharge" is normal current near a high-voltage conductor; and an "arc" is an unusual and undesired current. Similar breakdown can occur within any insulator, even within the bulk solid of a material. Even a vacuum can suffer a sort of breakdown, but in this case the breakdown or vacuum arc involves charges ejected from the surface of metal electrodes rather than produced by the vacuum itself.

15.7 DIELECTRIC BREAKDOWN PROPERTY

The term electrical breakdown can apply to the failure of an electric circuit. Alternatively, it may refer to a rapid reduction in the resistance of an electrical insulator that can lead to a spark jumping around or through the insulator.

If the dielectric material is fluid or gas, the electrical field in it can fully recover its insulating properties through the plasma channel interactions. Ceramic processed insulator is mixed with polymer or synthetic polymer to vary its dielectric property.

The theoretical dielectric strength is an intrinsic property of the bulk material and depends on the material composition and also on the configuration of the electrodes with which the field is applied. For a given configuration of dielectric material and electrodes, the minimum electric field that produces breakdown is the breakdown voltage in this particular set up; the maximum electric stress to the material is just before breakdown.

Table 15.4: Effect of dielectric strength

Factors	*Effect of dielectric strength*
Increased sample thickness	Decreases
Increased operating temperature	Decreases
Increased frequency	Decreases
Increased humidity	Decreases

In order to improve insulator performance, it is essential to understand the mechanisms of electrical breakdown in solid dielectrics. However, unlike the case for gases, electrical breakdown and conduction mechanisms in polymeric solids are less understood. Dielectric breakdown is the catastrophic failure of an insulating material under an external applied field resulting in mechanical damage and electrical conduction, depending upon the defect density of the solid material. Electrical breakdown testing of polymers for insulator applications has long been a subject of interest. Table 15.5 is a compilation of the dielectric strengths of some common polymers.

Table 15.5: List of Dielectric strengths of insulating polymers

Polymer	*Dielectric strengths*
Polyethylene (LD)	200
Polyethylene (HD)	200
Polyethylene (XL)	220
Polycarbonate	252
Polyester	300
Polyimide	280
Epoxy resin	25-45
Polypropylene	200

Table 15.6: Thermal conductivity and linear coefficient of thermal expansion for various materials at room temperature

Material	*Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)*	*Coefficient of thermal expansion (ppm/°C)*
Low density polyethylene (LDPE)	0.33	180–400
Polystyrene (PS)	0.04–0.14	90–150
High density polyethylene (HDPE)	0.45–0.52	106–198
Polyethylene terephthalate (PET)	0.29	117
Polypropylene (PP)	0.14	143
Polyetheretherketone (PEEK)	0.25	72–85
Polyvinyl chloride (PVC)	0.12–0.17	90–180
Polymethyl methacrylate (PMMA)	0.15–0.25	90–162
Polytetrafluoroethylene (PTFE)	0.25	126–216
Polycarbonate (PC)	0.19	122
ZnO	60	2.0–3.0
Fused SiO_2	1.5–1.6	0.4–0.5
$BaTiO_3$	6.2	6
Diamond	2,000	0.11–1.23
BN	29–300	1.1–4.3
Polybutylene terephthalate (PBT)	0.25	108–171
Epoxy	0.17–0.21	81–117
Silicone elastomer	0.17–0.26	270
SiC	85	4.1–4.7
AlN	150–220	2.5–5
BeO	300	5.5
Si_4N_3	86–120	2.7–3.1

15.8 DESIGN

The electrical breakdown of an insulator due to excessive voltage can occur in one of two ways:

- ***Puncture voltage:*** It is the voltage across the insulator (when installed in its normal manner) which causes a breakdown and conduction through the interior of the insulator. The heat resulting from the puncture arc usually damages the insulator irreparably.
- ***Flashover voltage:*** It is the voltage which causes the air around or along the surface of the insulator to break down and conduct, causing a ‘flashover’ arc along the outside of the insulator. They are usually designed to withstand this without damage.

Most high voltage insulators are designed with a lower flashover voltage than puncture voltage, so they will flash over before they puncture, to avoid damage. Dirt, pollution, salt and particularly water on the surface of a high voltage insulator can create a conductive path across it, causing leakage currents and flashovers. The flashover voltage can be more than 50% lower when the insulator is wet. High voltage insulators for outdoor use are shaped to maximize the length of the leakage path along the surface from one end to the other, called the creepage length, to minimize these leakage currents. To accomplish this the surface is moulded into a series of corrugations or concentric disc shapes. These usually include one or more sheds; downward facing cup-shaped surfaces that act as umbrellas to ensure that the part of the surface leakage path under the 'cup' stays dry in wet weather. Minimum creepage distances are 20–25 mm/kV, but must be increased in high pollution or airborne sea-salt areas.

Table 15.7: Typical number of disc insulator units for standard line voltages

Line voltage (kV)	34.5	46	69	92	115	138	161	196	230	287	345	360
Discs	3	4	5	7	8	9	11	13	15	19	22	23

15.9 PHYSICS OF CONDUCTION IN SOLIDS

Electrical insulation is the absence of electrical conduction. Electronic band theory (a branch of physics) says that a charge will flow if states are available into which electrons can be excited. This allows electrons to gain energy and thereby move through a conductor such as a metal. If no such states are available, the material is an insulator. Most (though not all, see Mott insulator) insulators have a large band gap. This occurs because the "valence" band containing the highest energy electrons is full, and a large energy gap separates this band from the next band above it. There is always some voltage (called the breakdown voltage) that will give the electrons enough energy to be excited into this band. Once this voltage is exceeded, the material ceases being an insulator, and charge will begin to pass through it. However, it is usually accompanied by physical or chemical changes that permanently degrade the material's insulating properties. Materials that lack electron conduction are insulators if they lack other mobile charges as well. For example, if a liquid or gas contains ions, then the ions can be made to flow as an electric current, and the material is a conductor. Electrolytes and plasmas contain ions and will act as conductors whether or not electron flow is involved.

15.10 ELECTRONIC CONDUCTION IN INSULATOR

Electronic conduction in insulating materials has been a subject of considerable interest in the quest to understand charge transport in the thin film layers of organic electronic devices. In typical dielectric materials, the electronic states near the Fermi level are usually localized states, and the electron wave functions decay exponentially over a distance known as the localization length. In constrast, metals have a high, generally uniform density of states, whereas semiconductors have well-separated conduction and valence bands (separated by a band gap). In a thin film transistor, there exists different junctions, metal-insulator, insulator-semiconductor, and semiconductor-metal, that must be fully understood to optimize the device performance characteristics. In this review, we will focus exclusively on conductor-dielectric interfaces. As we shall see, several theoretical models have been developed to explain conduction through these junctions.

15.11 USES

- Insulators are commonly used as a flexible coating on electric wire and cable. Since air is an insulator, in principle no other substance is needed to keep power where it should be. High-voltage power lines commonly use just air, since a solid (e.g., plastic) coating is impractical. However, wires which touch each other will produce cross connections, short circuits and fire hazards. In coaxial cable the centre conductor must be supported exactly in the middle of the hollow shield in order to prevent EM wave reflections. Finally, wires which expose voltages higher than 60 V can cause human shock and electrocution hazards. Insulating coatings help to prevent all of these problems.
- In high voltage systems containing transformers and capacitors, liquid insulator oil is the typical method used for preventing arcs. The oil replaces the air in any spaces which must support significant voltage without electrical breakdown. Other methods of insulating high voltage systems are ceramic or glass wire holders, gas, vacuum, and simply placing the wires with a large separation, using the air as insulation.
- Some wires have a mechanical covering which has no voltage rating, e.g., service-drop, welding, doorbell and thermostat. An insulated wire or cable has a voltage rating and a maximum conductor temperature rating. It may not have an ampacity (current-carrying capacity) rating, since this is dependent upon the surrounding environment (e.g. ambient temperature).
- In microelectronic components such as transistors and ICs, the silicon material is normally a conductor because of doping, but it can easily be selectively transformed into a good insulator by the application of heat and oxygen. Oxidized silicon is quartz, i.e. silicon dioxide.
- In electronic systems, printed circuit boards are made from epoxy plastic and fibreglass. The nonconductive boards support layers of copper foil conductors. In electronic devices, the tiny and delicate active components are embedded within nonconductive epoxy or phenolic plastics, or within baked glass or ceramic coatings.

15.12 TELEGRAPH AND POWER TRANSMISSION INSULATORS

Suspended wires for electric power transmission are bare, except where they enter buildings, and are insulated by the surrounding air. Insulating supports called insulators are required at the points at which they are supported by utility poles or pylons. Insulators are also required where the wire enters buildings or electrical devices, such as transformers or circuit breakers, to insulate the wire from the case. These hollow insulators with a conductor inside them are called bushings. The dangers posed by cranes touching bare electric power transmission wires has created the need for an insulating link to be used on cranes working near such wires.

15.13 INSULATION OF ANTENNAS

Often a broadcasting radio antenna is built as a mast radiator, which means that the entire mast structure is energized with high voltage and must be insulated from the ground. Steatite mountings are used. They have to withstand not only the voltage of the mast radiator to ground, which can reach values up to 400 kV at some antennas, but also the weight of the mast construction and dynamic forces. Arcing horns and lightning arresters are necessary because lightning strikes to the mast are common.

Guy wires supporting antenna masts usually have strain insulators inserted in the cable run, to keep the high voltages on the antenna from short circuiting to ground or creating a shock hazard. Often guy cables have several insulators, placed to break up the cable into lengths that are not submultiples of the transmitting wavelength to avoid unwanted electrical resonances in the guy. These insulators are usually ceramic and cylindrical or egg-shaped (see picture). This construction has the advantage that the ceramic is under compression rather than tension, so it can withstand greater load, and that if the insulator breaks the cable ends will still be linked.

These insulators also have to be equipped with overvoltage protection equipment. For the dimensions of the guy insulation, static charges on guys have to be considered. At high masts these can be much higher than the voltage caused by the transmitter, requiring guys divided by insulators in multiple sections on the highest masts. In this case, guys which are grounded at the anchor basements via a coil — or if possible, directly — are the better choice.

Feedlines attaching antennas to radio equipment, particularly twin lead type, often must be kept at a distance from metal structures. The insulated supports used for this purpose are called standoff insulators.

15.14 MOTT INSULATOR

Mott insulators are a class of materials that should conduct electricity under conventional band theories, but are insulators when measured (particularly at low temperatures). This effect is due to electron-electron interactions which are not considered in conventional band theory. Mott insulators are of growing interest in advanced physics research, and are not yet fully understood. They have applications in thin-film magnetic hetero structures and high-temperature superconductivity, for example.

15.15 TOPOLOGICAL INSULATOR

A topological insulator is a material that behaves as an insulator in its interior or bulk while permitting the movement of charges (metallic) on its surface. In the bulk of a topological insulator the electronic band structure resembles an ordinary band insulator, with the Fermi level falling between the conduction and valence bands. On the surface of a topological insulator there are special states that fall within the bulk energy gap and allow surface metallic conduction. Carriers in these surface states have their spin locked at a right-angle to their momentum (spin-momentum locking or topological order). At a given energy the only other available electronic states have different spin, so the "U"-turn scattering is strongly suppressed and conduction on the surface is highly metallic. These states are characterized by an index (known as Z2 topological invariants) similar to the genus in topology, and are an example of topologically ordered states.

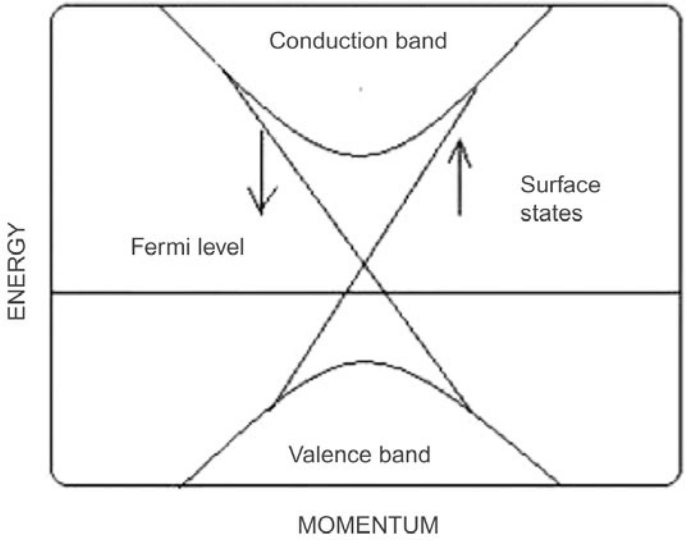

Fig. 15.3: Topological insulator

15.16 PROPERTIES AND APPLICATIONS OF TOPOLOGICAL INSULATOR

The surface states of a 3D topological insulator is a new type of 2DEG (two dimensional electron gas) where electron's spin is locked to its linear momentum. The topological surface states differ from graphene due to the locking of spin and momentum. Spin momentum locking or topological order allows topological surface states to host majorana particles if superconductivity is induced on the surface of 3D topological insulators via proximity effects.

Factors to be considered for effective insulation

Insulation performance is influenced by many factors, the most prominent of which include:

- ➜ Thermal conductivity
- ➜ Insulation thickness
- ➜ Specific heat capacity
- ➜ Surface emissivity
- ➜ Density
- ➜ Thermal bridging

It is important to note that the factors influencing performance may vary over time as material ages or environmental conditions change.

15.17 APPLICATIONS

Clothing

Clothing is chosen to maintain the temperature of the human body. To offset high ambient heat, clothing must enable sweat to evaporate (cooling by evaporation). When humans anticipate high temperatures and physical exertion, the billowing of fabric during movement creates air currents that increase evaporation and cooling. A layer of fabric insulates slightly and keeps skin temperatures cooler than otherwise. To combat cold, evacuating skin humidity is still essential while several layers of materials with different properties are necessary to simultaneously achieve this goal while matching one's internal heat production to the heat losses that occur. The key is layering for different purposes, as heat loss occurs due to wind, radiation of heat into space and conductive bridging. The latter is most apparent in footwear where insulation against conductive heat loss is most important.

Buildings

Maintaining acceptable temperatures in buildings (by heating and cooling) uses a large proportion of global energy consumption. When well insulated, a building:

- is energy-efficient, thus saving the owner money.
- provides more uniform temperatures throughout the space. There is less temperature gradient both vertically (between ankle height and head height) and horizontally from exterior walls, ceilings and windows to the interior walls, thus producing a more comfortable occupant environment when outside temperatures are extremely cold or hot.
- has minimal recurring expense. Unlike heating and cooling equipment, insulation is permanent and does not require maintenance, upkeep, or adjustment.

Many forms of thermal insulation also reduce noise and vibration, both coming from the outside and from other rooms inside a building, thus producing a more comfortable environment. Window insulation film can be applied in weatherization applications to reduce incoming thermal radiation in summer and loss in winter. In industry, energy has to be expended to raise, lower, or maintain the temperature of objects or process fluids. If these are not insulated, this increases the energy requirements of a process, and therefore the cost and environmental impact.

Mechanical systems

Space heating and cooling systems distribute heat throughout buildings by means of pipe or ductwork. Insulating these pipes using pipe insulation reduces energy into unoccupied rooms and prevents condensation from occurring on cold and chilled pipe work. Pipe insulation is also used on water supply pipe work to help delay pipe freezing for an acceptable length of time.

Spacecraft

Insulation for applications on spacecraft must be light-weight. In particular, spacecraft must be insulated against radiative heating from thermal radiation as no means exist in space for convective cooling by the atmosphere. Outside the Earth's atmosphere, radiated energy from the Sun is greater than on Earth, and all surfaces exposed heat up quickly. Thermal radiation insulation often consists of multi-layer insulation using special paints, foams and layers of metal.

Launch and re-entry place severe mechanical stresses on spacecraft, so the strength of an insulator is critically important (as seen by the failure of insulating foam on the Space Shuttle Columbia). Re-entry through the atmosphere generates very high temperatures because of friction against air at high speeds. Insulators must meet demanding physical properties beyond their thermal transfer retardant properties, e.g. reinforced carbon-carbon composite nose cone and silica fibre tiles of the space shuttle.

15.18 PLANNING

How much insulation a house should have depends on building design, climate, energy costs, budget, and personal preference. Regional climates make for different requirements. Building codes specify only the bare minimum; insulating beyond what code requires is often recommended. Formation of house depends on the climatic situation, so, in this regards by using appropriate insulator house is made according to weather.

The insulation strategy of a building needs to be based on a careful consideration of the mode of energy transfer and the direction and intensity in which it moves. This may alter throughout the day and from season to season. It is important to choose an appropriate design, the correct combination of materials and building techniques to suit the particular situation.

To determine whether you should add insulation, you first need to find out how much insulation you already have in your home and where. A qualified home energy auditor will include an insulation check as a routine part of a whole-house energy audit.

15.19 CLIMATE

Cold climates

In cold conditions, the main aim is to reduce heat flow out of the building. The components of the building envelope – windows, doors, roofs, walls and air infiltration barriers – are all important sources of heat loss; in an otherwise well insulated home, windows will then become an important source of heat transfer. The resistance to conducted heat loss for standard glazing corresponds to an *R*-value of about 0.17 W/m^2/Ko (compared to 2-4 W/m^2/Ko for glasswool batts). Losses can be reduced by good weatherisation, bulk insulation and minimising the amount of non-insulative (particularly non-solar facing) glazing. Indoor thermal radiation can also be a disadvantage with spectrally selective (low-e, low-emissivity) glazing. Some insulated glazing systems can double to triple *R* values.

Hot climates

In hot conditions, the greatest source of heat energy is solar radiation. This can enter buildings directly through windows or it can heat the building shell to a higher temperature than the ambient, increasing the heat transfer through the building envelope. The Solar Heat Gain Co-efficient (SGHC) (a measure of solar heat transmittance) of standard single glazing can be around 78-85%. Solar gain can be reduced by adequate shading from the sun, light coloured roofing, spectrally selective (heat-reflective) paints and coatings and various types of insulation for the rest of the envelope. Specially coated glazing can reduce SHGC to around 10%. Radiant barriers are highly effective for attic spaces in hot climates. In this application, they are much more effective in hot climates than cold climates. For downward heat flow, convection is weak and radiation dominates heat transfer across an air space. Radiant barriers must face an adequate air-gap to be effective.

If refrigerative air-conditioning is employed in a hot, humid climate, it is particularly important to seal the building envelope. Dehumidification of humid air infiltration can waste significant energy. On the other hand, some building designs are based on effective cross-ventilation instead of refrigerative air-conditioning to provide convective cooling from prevailing breezes.

QUESTIONS

1. What is relative permeability?
2. Using clay how insulator is prepared?

3. What is the analogy between conductor dielectric voltage and water channel pipe wall pressure?
4. What is the dielectric breakdown property?
5. Depending on factors, what are the effects of dielectric strength?
6. What is the relationship between thermal conductivity and linear coefficient of thermal expansion?

FURTHER READING

Bernevig, B. Andrei, Taylor L. Hughes and Shou-Cheng Zhang (2006.). Quantum Spin Hall Effect and Topological Phase Transition in HgTe Quantum Wells. *Science,* **314(5806):** 1757–1761. doi:10.1126/science.1133734. PMID 17170299. http://www.sciencemag.org/cgi/content/abstract/314/5806/1757. Retrieved 2010-03-25.

Burgess-Beusse, B. et al. (2002). The insulation of genes from external enhancers and silencing chromatin. *Proc. Natl Acad. Sci. USA*, **9(Suppl 4):** 16433–16437. doi:10.1073/pnas.162342499. PMC 139905. PMID 12154228. http://www.pubmedcentral.nih.gov/articlerender.fcgi?tool=pmcentrez&artid=139905

Frank P. Incropera and David P. De Witt (1990). Fundamentals of Heat and Mass Transfer (3rd ed.). John Wiley & Sons.

Hasan, M.Z. and Kane, C.L. (2010). Topological Insulators. *Review of Modern Physics*, **82(4):** 3045. Bibcode 2010RvMP...82.3045H. doi:10.1103/RevModPhys.82.3045. http://link.aps.org/doi/10.1103/RevModPhys.82.3045. Retrieved 2010-03-25.

Hsieh, D., Qian, D., Wray, L., Xia, Y., Hor, Y.S., Cava, R.J. and Hasan, M.Z. (2008). A Topological Dirac insulator in a quantum spin Hall phase. *Nature*, **452(9):** 970–974. Bibcode 2008Natur.452..970H. doi:10.1038/nature06843. PMID 18432240. http://www.nature.com/nature/journal/v452/n7190/full/nature06843.html. Retrieved 2010.

Hsieh, D., Xia, Y., Qian, D., Wray, L., Meier, F., Dil, J. H., Osterwalder, J., Patthey, L., Fedorov, A.V., Lin, H., Bansil, A., Grauer, D., Hor, Y. S., Cava, R. J. and Hasan, M. Z. (2009). Observation of Time-Reversal-Protected Single-Dirac-Cone Topological-Insulator States in Bi2Te3 and Sb2Te3. *Physical Review Letters* **103 (14):** 146401. Bibcode 2009PhRvL.103n6401H. doi:10.1103/PhysRevLett.103.146401. PMID 19905585. http://link.aps.org/doi/10.1103/PhysRevLett.103.146401. Retrieved 2010-03-25.

Kane, C.L. and Moore, J.E. (2011). Topological Insulators. *Physics World*, **24:** 32. http://www.physics.upenn.edu/~kane/pubs/p69.pdf.

Konig, Markus, Steffen Wiedmann, Christoph Brune, Andreas Roth, Hartmut Buhmann, Laurens W. Molenkamp, Xiao-Liang Qi and Shou-Cheng Zhang (2007). Quantum Spin Hall Insulator State in HgTe Quantum Wells. *Science*, **318(5851):** 766–770. doi:10.1126/science.1148047. PMID 17885096. http://www.sciencemag.org/cgi/content/abstract/318/5851/766. Retrieved 2010-03-25.

Pankratov, O.A., Pakhomov, S.V., and Volkov B.A. (1986). Supersymmetry in Heterojunctions: Band-inverting Contact on the Basis of Pb(1-x)Sn(x)Te and Hg(1-x)Cd(x)Te. *Solid State Communications*, **61(2):** 93–96. doi:10.1016/00381098(87)90934-3. http://www.sciencedirect.com/science/article/pii/0038109887909343. Retrieved 2011-06-15.

PART III

Clays in the Environment

CHAPTER

16

BENEFICIAL AND HAZARDOUS ASPECTS OF CLAYS IN NATURE: A BRIEF OVERVIEW

Of the different types of reactions taking place continuously in the environment, some are activating reactions that contribute to environmental pollution and contaminations. Other reactions that resist environmental pollution or contamination are the neutralising reactions. The clay minerals, being very stable in the condition prevailing at the surface of earth, generally do not participate in activating reactions, though the clay particles from waste dumps may have negative impacts on the air, soil and water sources of surrounding regions. Clay minerals can remove the ions of pollutants and contaminants from solutions. This property enables them to play very important roles in many natural neutralising reactions and facilitate their applications in many pollution control measures.

16.1 INTRODUCTION

Environment is the sum total of all the surroundings of a living organism, and it essentially consists of all the physical, chemical and biotic factors acting upon that organism. The environment in which we live includes other living organisms (different types of plants and animals), inorganic matters (air, water, soil etc.) and natural processes, which provide conditions for our survival, development and growth. The study of the environment is a multidisciplinary approach; and numerous scientists of various disciplines throughout the world are actively engaged in studying the different aspects of the environment, especially the human impacts on its integrity. Consequently the terminologies related to different aspects of the environment vary greatly in the works of

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different authors. The ambiguity thus arising for the definition of the terms environmental pollution, contamination, environmental degradation etc. may be confusing for the students. The definitions of those terms and their brief explanation are therefore presented here.

Environmental pollution: It is the addition of any substance (solid, liquid or gas) or any form of energy (heat, sound etc.) to the environment at a rate faster than it can be dispersed, diluted or decomposed. As a result it gradually accumulates with time and causes damage to the environment when the accumulation crosses a certain limit.

The substance or energy introduced into the environment that has undesired effects is known as a *pollutant*. A pollutant may cause long- or short-term damage by changing the growth rate of plant or animal species, or by interfering with human amenities, comfort, health or property values.

The three important components of the environment, i.e. the air, water and soil, can be polluted by the anthropogenic activities.

Air pollution is the release into the atmosphere of various gases, finely divided solids, or finely dispersed liquid aerosols at rates that exceed the natural capacity of the environment to dissipate and dilute or absorb them. These substances may reach concentrations in the air that cause undesirable health, economic or aesthetic effects.

Water pollution is the release of substances into surface water bodies or subsurface groundwater to the point where the substances interfere with the beneficial use of the water or with the natural functioning of ecosystems.

Soil pollution is the deposition of solid or liquid materials in the soil in a manner that can decrease the fertility of the soil, destroy the plants or threaten public health.

Environmental contamination: It is the unintended presence or introduction of biological, chemical, physical or radiological substance *which are normally absent in the environment*. These substances, known as *contaminants*, can adversely affect living organisms through air, water, soil, food etc. when present in sufficient concentration.

It is to be noted here that contaminants are not normally present in the environment and generally introduced by anthropogenic activities. But pollutants may be present naturally in the environment in trace amounts, and is harmful only when its concentration in nature crosses a particular limit. For example, carbon monoxide is a contaminant, which is not present in air in normal condition. But carbon dioxide is a pollutant which is naturally present in the air, and has harmful effect on the environment when its concentration crosses a certain limit.

Environmental degradation: It is the deterioration of the environment through change or disturbance in the quality or quantity of natural resources such as air, water and soil which may bring about the destruction of ecosystems, extinction of wildlife and human health hazards. It is a more generalized term that includes any physical or chemical change in the environment perceived to be harmful or undesirable. Depletion of the freshwater sources and introduction of a harmful chemical in water are both considered as environmental degradation, while only the latter is considered as environmental pollution.

Clays, like most other natural substances, have some beneficial and some hazardous impacts on the environment. As described in Part I, clays have a tendency to adsorb and immobilize ions. This property enables clays to remove ions of pollutants and contaminants from leachates and waste water, thus reducing pollution and contamination. It also facilitates the use of clays in different pollution control measures like carriers of pesticides, liners in waste disposal etc. Clays can also be used in nuclear waste management: clay buffers are built from smectite-rich clays into which the containers of radioactive wastes can be safely disposed (Pusch, 2006).

On the other hand, tendency of the clays to be suspended easily in air (owing to their very fine grainsize), and their property to absorb water and produce plastic mass etc. may cause environmental degradation in certain circumstances.

The harmful effects of clay mining and the uses of clays to resist pollution are described elaborately in the next chapters of Part III. This chapter explains the geochemical processes involved in pollution and contamination, and the roles of clays in those processes.

16.2 ACTIVATING AND NEUTRALIZING REACTIONS AND THEIR CONTROLLING FACTORS

The different types of inorganic and organic waste materials dumped from the mines, factories, construction sites etc. come into contact and react with different natural substances like water (rainwater or surface runoff), atmospheric oxygen, carbon dioxide etc. Some of the reactions are *activating reactions* in which a mineral or an organic material reacts with the natural substances to produce one or more pollutant and/or contaminant. Others are *neutralising reactions* in which one or more reactants (a mineral or organic material or any natural substances) react with the pollutant and/or contaminant produced by activating reactions and transforms them into some non-detrimental form, thus decreasing their quantities in nature and tending to prevent pollution/contamination. Let x be the *net quantity* of a particular pollutant or contaminant X at a certain point of time. It depends on:

(i) Quantity of X produced in the reaction site by the activating reactions [x_α] and
(ii) Quantity of X removed from water by the neutralising reactions [x_ν]

Therefore:

$$x = x_\alpha - x_\nu \tag{16.1}$$

For example, sphalerite (ZnS), a common mineral present in the waste dumps of sulphide mines, is oxidised by atmospheric oxygen to produce zinc sulphate.

$$ZnS + 2O_2 = ZnSO_4 \tag{16.2}$$

Zinc sulphate, being a highly soluble substance, is a potential pollutant of water and soil. Therefore reaction 17.2 is an activating reaction.

The dissolved $ZnSO_4$ thus produced reacts with calcite ($CaCO_3$) to produce smithsonite ($ZnCO_3$).

$$ZnSO_4 + CaCO_3 = ZnCO_3 + CaSO_4 \tag{16.3}$$

Smithsonite is nearly insoluble in water and precipitates from the solution; thus Zn^{++} is removed from water. Nuttal and Younger (2000) found a 22% average reduction in zinc concentration in an open system over a retention time of 14 hours. Therefore reaction 17.3 is a neutralising reaction.

The net quantity of Zn^{++} thus produced is transported and accumulates into the water bodies or soil of surrounding areas; and brings about pollution of water or soil when its proportion crosses a permissible limit.

The activating and neutralising reactions may take place in the waste disposal sites of mines, factories, construction sites etc. The excavated area in the mine may also act as a reaction site, where water percolates and reacts with the minerals of newly exposed rock layers. All these are the *external reaction sites,* from which the pollutants or contaminants are produced and transported to soil or water bodies of surrounding areas, causing pollution or contamination of soil or water respectively. In addition, soil and water bodies themselves become the *internal reaction sites* of activating and neutralising reactions when the unreacted waste materials are transported to them.

16.2.1 Reactions in an Open System and Total Number of Reactable Moles

Let us consider the following hypothetical reaction.

$$aA + bB = cC + dD \tag{16.4}$$

Here a and b moles of the two reactants, A and B respectively, produce c and d moles of the two products C and D respectively. In a close reaction system where no reactant or product can enter from or escape to the surrounding, the reaction will be reversible, i.e. a backward reaction will simultaneously produce A and B from C and D. When accumulation of C and D reaches a certain limit, the rate of forward reaction and backward reaction will be same, and the concentrations of the reactants and products in the system will remain constant unless pressure, temperature etc. changes.

An open reaction system exchanges reactants and/or products with the surrounding. Here the reaction continues until one of the reactants is exhausted. Let X be a reactant having molecular weight M_X, W_X be the amount of X in the reaction system in gram, and x is the number of molecules of X participating in the reaction. Then $\frac{W_X}{xM_X}$ determines the following:

(i) The residual quantity of that reactant X, if any, in the reaction system after the reaction is over.

(ii) The quantity of products produced in the reaction.

The expression $\frac{W_X}{xM_X}$ is the ***Total Number of Reactable Moles*** or ***TNRM*** of X (Mukhopadhyay and Ghosh, 2010a). In the hypothetical chemical reaction 17.4, if the molecular weights of the four substances are M_A, M_B, M_C and M_D respectively, and W_A gram of A and W_B gram of B are present in the reaction system, then aM_A gram of A reacts with bM_B gram of B to produce cM_C and dM_D grams of C and D respectively.

Then the following situations are possible:

Case I: $$\frac{W_A}{aM_A} = \frac{W_B}{bM_B} = k \text{ (say)}$$

W_A grams of A will react with W_B grams of B. At the end of the reaction, the residual quantities of both reactants in the reaction system will be zero. kcM_C gram of C and kdM_D gram of D will be produced by the reaction.

Case II: $$\frac{W_A}{aM_A} < \frac{W_B}{bM_B}$$

W_A grams of A will react with $W_A \frac{bM_B}{aM_A}$ grams of B. The reaction will continue until the entire quantity of A is exhausted in the reaction system. $\left(W_B - W_A \frac{bM_B}{aM_A}\right)$ gram of B will remain unreacted. $W_A \frac{cM_C}{aM_A}$ gram of C and $W_A \frac{dM_D}{aM_A}$ gram of D will be produced by the reaction.

Similarly, when $\frac{W_B}{bM_B} < \frac{W_A}{aM_A}$, the reaction will continue until the entire quantity of B is exhausted in the reaction system.

So we can infer from the above discussion that *if the TNRM of one of the reactants in the open reaction system is less than that of the other(s), then all of the former will be used up in the reaction and some part of the other(s) will remain unreacted in the system.* Therefore an activation or neutralisation reaction between a mineral and water in an open system will continue until either that mineral or water is exhausted in the reaction system.

Example: Pyrite is one of the most abundant mineral of the sulphide deposits. It may also be present in coal seams or in the shale beds associated to them. Being insoluble in water, it does not increase the iron content of water and degrade water quality. But at the surface of earth it can be naturally oxidised in presence of atmospheric oxygen and water, as shown in the following activating reaction

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4 \qquad (16.5)$$

240 grams of pyrite (FeS_2) reacts with 224 grams of oxygen and 36 grams of water to produce 304 grams of ferrous sulphate ($FeSO_4$) and 196 grams of sulphuric acid (H_2SO_4). Ferrous sulphate, a water-soluble salt of iron, increases the iron content and sulphuric acid decreases the pH of water; both are detrimental to the water quality.

In a reaction system with 480 grams of pyrite, 500 grams of oxygen and 100 grams of water, TNRM of the three reactants are: pyrite: 480/240 = 2, oxygen: 500/224 = 2.23, water: 100/36 = 2.77. When the reaction is complete, pyrite, having the least TNRM, will be exhausted when 52 grams of oxygen and 28 grams of water remain unreacted.

Pyrite-rich layers are generally situated under a thick sequence of soil and rocks. Depending on the position of the pyrite-rich layer with respect to the water table, some amount of ground water may permeate into them, but the quantity of atmospheric oxygen coming in contact of these layers is very small. So the quantity of ferrous sulphate and sulphuric acid produced by the oxidation of pyrite is very small and that depends mainly on the molar quantity of oxygen available in the reaction site, and most of the pyrite and much of the water present in the reaction system remain unreacted due to the dearth of oxygen. But mining activity, through excavation and removal of overburden, exposes to atmospheric oxygen and water the pyrite present in rock layers, waste heaps, mineral dump etc. The total quantity of sulphuric acid produced will depend on the TNRM of pyrite or water, whichever is less. For example, in a surface water body where pyrite is transported from waste dump, the quantity of sulphuric acid produced depends on the supply of pyrite in it, until the ratio of pyrite and water exceeds 20:3 (i.e. 240:36). Similarly, the acid produced in a waste heap rich in pyrite depends on the quantity of water leaching through it.

16.2.2 Constraints of Reactions in an External Reaction Site

An external reaction site (like a waste dump) largely behaves as an open system, because the precipitated water penetrates into it, reacts with activating and neutralising minerals, and flows out of the systems with the net quantity of pollutant or contaminant produced. In this case, the reaction system extends from the surface of the dump to the depth of penetration of water; and the reaction between a mineral and water will be restricted by the TNRM of water in the reaction system. For this reason, more pollutant or contaminant will be leached out from the waste dump in the rainy season than in the dry season.

Besides, the permeability of the waste materials also plays an important role – greater is the permeability, greater amount of water will penetrate into the dump and as a consequence, larger will be the TNRM of water in the reaction system. If the surface of waste dump is covered by fine grained materials of less permeability (like clay), a large part of water falling on will not penetrate into the reaction system. For this reason, clay can be effectively used in liners of waste disposal.

Constraints of Reactions in an External Reaction Site

An internal reaction site like a pond or lake may appear as a close system, but it largely acts as an open system. When a mineral particle is transported to such a reaction site, its outermost part will react with the water. The soluble pollutant thus produced will be dissolved and defused in the water, exposing a fresh surface for reaction until the whole particle is exhausted. Therefore reaction between water and an activating or neutralising mineral will be restricted by the availability of that mineral – the quantity of it transported in the water body. Other factors remaining same, greater is the distance of the surface water body from the waste dump, less will be the amount of reactants transported to it. The surface water bodies nearer to the waste dump will therefore be more polluted.

16.3 THE ROLE OF CLAY MINERALS IN ACTIVATING AND NEUTRALIZING REACTIONS

16.3.1 Clay Minerals as Activating Agents

For a substance to act as an activating agent, it must react with natural substances to produce one or more soluble substances that increase the cation and anion contents of water. For example, zinc sulphide is an activating agent as it produces highly soluble zinc sulphate which increases Zn^{++} into water. But the clay minerals rarely act as activating agents in nature, as explained below.

Each mineral is stable within certain ranges of pressure and temperature and a definite chemical environment. The minerals formed in a high pressure, high temperature and reducing environment deep inside the Earth's crust may be uplifted by some geological processes and brought to the Earth's surface, where the physico-chemical conditions are much different, characterised by lower temperature and pressure, higher free water and free oxygen. Because of these differing conditions, those minerals will produce new minerals that are stable under conditions at or near the surface.

As shown in Table 1.4 (Part I, Chapter 1), clay minerals are among the most stable minerals in the condition prevailing at the Earth's surface. Therefore they are not likely to react with water or atmospheric gases to produce other substances. Moreover, they are insoluble in water (though may create a colloid solution in water for their extremely fine grainsize), thus incapable of changing the water quality. One clay mineral may be transformed to another by processes like diagenesis, low-grade metamorphism etc. but that does not involve liberation of harmful materials in nature. So they rarely act as activating agents.

16.3.2 Clay Minerals as Neutralizing Agents

As discussed in the internal structure of clays in Part I, many clay minerals have t-o-t-c structures. In these clays, the c-layer in between two t-o-t layers has a series of cationic sites with 12-fold coordination number. Some of those cationic sites are filled up by interlayer cations like Na^+, Ca^{2+}, Mg^{2+} etc. while the others are vacant. The metallic pollutants and contaminants like Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+} etc. enter the c-layer of these clays by substituting the interlayer cations or by occupying the vacant cationic sites. Thus the heavy metals and other cations can be removed by the clays from a solution. These clay minerals therefore act as neutralising agents that naturally reduce or tend to reduce pollution and contamination. The metal cation adsorption capacity of clay minerals can be enhanced artificially by organic complexation as well as hydroxyl interlayering and pillaring. In addition to removal of heavy metals and other inorganic cations, clay minerals can also remove from the water the organic cations present in waste proteins, biological toxins, antibiotics etc. Non-ionic organic pollutants, anionic contaminants present in fertilizers and pesticides and organisms like viruses can also be removed by clay (Churchman et al., 2006).

Leachates form by the interaction of rainwater with the waste materials of mine or industrial waste dumps. The constituents of the leachates depend on the compositions of the waste materials in the waste dumps, and some of them may be potential pollutants or contaminants of water. When the leachate flows over the ground surface, it passes through the soil and some of the dissolved substances present in it are removed by the clay minerals present in the soil. Thus fewer amounts of pollutants and contaminants reach the surface water bodies. Therefore the surface water bodies distant from the waste dump are generally less polluted or contaminated than those that are close to the waste dump.

Similarly, when a part of leachate percolating downward through the vadose zone passes through the clay-rich subsurface layers, the clay minerals remove a part of dissolved substances from it, preventing or decreasing the pollution or contamination of ground water.

The clay minerals present in the aquifer and the wall of surface water bodies may also remove some dissolved substances from the water and improve the qualities of ground water and surface water respectively.

These neutralising properties of clay minerals facilitate their use to resist water and pollution. Furthermore, the waste materials may be prevented from coming in contact with water by burying them under soil or covering them by a thick layer of clays – the absorption and swelling properties of clays resist the penetration of water in the reaction system and significantly decrease the TNRM of water in it. For this reason, clays can be applied effectively to build barriers/linings that resist spreading of pollutants and contaminants from waste dumps, to clear waste water and leachate of the harmful cations, and to protect the soil of agricultural lands from the harmful effects of chemical fertilizers and pesticides. These applications of clays are described in the next chapters.

16.4 ENVIRONMENTAL DEGRADATION BY CLAYS

In order to have a comprehensive idea of the negative impacts of clays on the environment, the following two phenomena should be understood separately:

(a) During the mining and beneficiation of CLAYS, environmental degradation may take place.
(b) During the mining of ANY ECONOMIC MATERIAL (any metallic ores, non-metallic substances or fuel), the clays present in host rock, country rock and overburden may cause environmental degradation. The clay present in the waste dumps of construction sites or industrial areas have similar impacts on the environment.

Most clay mines are surface mines, in which the miner and/or his machinery work in an excavated void which is open to the sky. The surface mines are of following types:

Open-pit mine: In this type of surface mines, the overburden is removed from the mine and dumped to a disposal area. The desired material is worked from stepped horizontal benches. Each bench is separated from the adjacent benches by vertical shelves. The slope angle ranges 50°–70°. Since clay layers are softer than most materials and the exposed parts become very slippery in rainy season, a smaller slope angle is required to maintain stability of the mine.

Open-cast mines: They are surface mines in which the stripped overburden is not removed from the mine to be dumped in a separate disposal area, but is "cast" (i.e. hauled and dumped) inside the mine from where the desired material is already worked.

The following operations are carried out in the mining of clays:

(a) Stripping of overburden, i.e. excavation and removal of the vegetation, soil and layers of sediments overlie the clay bed
(b) Mining of the clay
(c) Disposal of waste materials
(d) Beneficiation of the clay, i.e. partial removal of impurities and giving it a desired form.

All types of surface mines, including the clay mines, have some negative impacts on the environment in each of the three stages of operation, as briefly explained below.

(i) Stripping of overburden causes destruction of a large amount of vegetation, and loss of top soil. This severely affects the environment of the surrounding areas.

(ii) During excavation of clay from the mine, especially in the deeper levels, a part of the aquifer may be removed, leading to loss of ground water through increased evaporation, and causing serious hindrance to groundwater circulation. It also increases the possibility of pollution of ground water by exposing the aquifer to the pollutants (Younger, 2003). Even when the excavation is not deep enough to reach the water table or affect the aquifer, it intercepts the surface runoff and interflow, leading to wastage of water and desiccation of surrounding surface water bodies (Mukhopadhyay and Ghosh, 2011a and references therein).

(iii) The mine wastes, when dumped at a different place (i.e. in case of open pit mines), destroy more vegetation and top soil. If the waste materials contain any harmful chemicals, that may be leached out from the waste dump in the rainy season and pollute the surface water bodies and soil of surrounding areas.

In addition to the above environmental degradations that are common to all types of surface mines, the clay mines in particular may cause air pollution. Clays are finest of all sedimentary particles, and owing to their fine grainsize, they are very light and easily airborne. For this reason, the fine clay particles are suspended easily in the air during mining and beneficiation. That may cause respiratory troubles and other health hazards to the mine workers and the inhabitants of surrounding areas. A detailed account of environmental degradation during clay mining and beneficiation is given in Chapter 8 of this book.

16.5 ENVIRONMENTAL DEGRADATION BY CLAYS FROM WASTE DUMPS

In any mining operation, overburden materials and tailings are disposed in the waste dumps. Many construction works necessitate excavation and removal of soil and sediment layers from a large area and dumping them to a nearby place. Clays are the major components of these waste dumps. Clays may also be present in some types of industrial wastes. Different components of the waste dump may have different impacts on the water, soil and air of the surrounding regions. The impacts of clays of the waste dump on the environment are given below.

(i) Of all types of sedimentary particles present in the waste dumps, the clays are the lightest and most easily suspended into the air. The airborne clay particles may be carried to far-off places, and affect the health of the inhabitants of surrounding regions. Respiratory diseases such as *silicosis* can result from long-term exposure to clay dusts.

(ii) Clay particles are easily transported from the waste dumps by air and rainwater, while the coarser particles are left back. The transported clay particles settle on the soil. They may block the soil pore spaces and absorb a considerable amount of infiltrated rainwater, and less amount of water is available for surface runoff, interflow and groundwater recharge. In addition, the moist clay particles form a cohesive plastic mass in the soil that hinders the lateral and vertical movement of water in the unsaturated zone. Less lateral flow of water brings about further decrease in the throughflow and interflow, contributing to desiccation of surface water sources. Decrease in the vertical movement of water, on the other hand, further decrease groundwater recharge that leads to fall of water table.

(iii) A large amount of clay particles, when deposited on a small stream or pond, may block it or fill it up, leading to depletion of water sources.

Concluding Remarks

Rapid growth in the population and concomitant industrial development and urbanisation has given rise to rampant mining activities, establishment of new industries and extensive constructional works in different parts of the world. All these have brought about disposal of a huge quantity of waste materials, which are the sources of all types of pollutants and contaminants and are therefore serious threats to the Earth's environment. In this context, extensive researches are going on throughout the world to find out effective but economic means to prevent environmental pollution and contamination from the waste materials. Clays, owing to their stability, distinctive properties, abundance and easy availability in nature, may be applied effectively to overcome some of the appalling environmental problems coming from the wastes. Researchers are therefore increasingly depending on clays and clay derivatives to invent possible ways of pollution control. The utilization of a particular type of clay for the control of a particular class of pollutants or contaminant is gradually attaining its own maximum stage of development. With the passage of time, further industrial developments may give rise to new environmental threats or exacerbate the present ones, necessitating further researches for finding out new applications of the clays for environmental protection.

At the same time, growth of the civilization calls for a greater utilization of clays and its derivatives in the industries, and substitution of metals with them. This will give rise to increase of clay mining and associated environmental degradation, necessitating simultaneous researches for minimizing the harmful effects of clay mining.

QUESTIONS

1. Is it justified to use the terms environmental pollution, contamination and degradation interchangeably? Explain with examples.
2. Is it possible for a substance to act as an activating agent in a particular circumstance, and as a neutralizing substance in another? Cite suitable example in support of your answer.
3. In a waste dump, metallic sulphides react with rain water to form soluble sulphates, which leach out to pollute the surrounding water bodies. The TNRM of which reactant will be the main controlling factor in this activating reaction? Explain.
4. In a water body, metallic sulphides leach out from a nearby waste dump and react with water to form soluble sulphates and pollute the water. The TNRM of which reactant will be the main controlling factor in this activating reaction? Explain.
5. Explain why the clay minerals hardly ever act as activating agents.
6. Both clay mineral and $CaCO_3$ present in the rock layers or soil can remove sulphate pollutants from leachates. Which of these two neutralizing agents do you think is more appropriate from the environmental point of view? Explain with reasons.
7. What is the role of the swelling property of smectite clays in environmental protection?
8. An overburden dump comprises different materials like gravels, sands, silts, clays etc. of which air pollution is caused by clays. Which property of clays is responsible for it?

FURTHER READING

Churchman, G.J., Gates, W.P., Theng, B.K.G. and Yuan, G. (2006). Clays and clay minerals for pollution control. *In:* Handbook of Clay Science. Bergaya, F., Theng, B.K.G. and Lagaly, G. (eds) Elsevier Ltd., 625–675.

G. Yuan Encyclopædia Britannica Online, s. v. “pollution”, last accessed June 01, 2012, http://www.britannica.com/EBchecked/topic/468070/pollution.

Fetters, C.W. (1988). Applied Hydrogeology. 2nd ed. Merril Publishing Company, U.S.A.

Freeze, R.A. and Cherry, J.A. (1979). Groundwater. Prentice Hall Inc., New Jersey.

Grim, R.E. (1968). Clay mineralogy. 2nd ed. McGraw-Hill, New York.

Manahan, S.E. (2000). Environmental Chemistry. 7th ed. CRC Press, Boca Raton FL.

Mukhopadhyay, L. and Ghosh, B. (2010b). Mining induced water pollution – impact on traditional economic livelihood: an analytical framework. *In:* 4th World Congress of Environment and Resource Economics at UQAM, Montréal, Canada. Available in: http://www.webmeets.com/files/papers/WCERE/2010/1219/Lekha-%20Bhaskar-water%20pollution-Revised-%20june23.pdf

Mukhopadhyay, L. and Ghosh, B. (2011a). Mining induced desiccation and consequent impact on traditional economic livelihood – An analytical framework. *In:* XIII Annual Bioecon Conference at IHEID, Geneva, Switzerland. Available in: www.bioecon-network.org/pages/13th_2011/Mukhopadhay.pdf

Nuttall, C.A. and Younger, P.L. (2000). Zinc removal from hard, circum-neutral mine waters using a novel closed-bed limestone reactor. *Water Research*, **34(4):** 1262–1268.

Pusch, R. (2006). Clays and nuclear waste management. *In:* Handbook of Clay Science. Bergaya, F., Theng, B.K.G. and Lagaly, G. (eds). Elsevier Ltd., 703–716.

Pusch, R. (1994). Waste Disposal in Rock. Developments in Geotechnical Engineering. Elsevier, Amsterdam.

Steger, H.F. and Desjardins, L.E. (1980). Oxidation of sulfide minerals: v. galena, sphalerite and chalcocite. *Canadian Mineralogist*, **18:** 365–372.

Younger, P.L. (2003). Impacts of mining on physical hydrogeology. *In:* 2nd Image-Train Advanced Study Course. 2003, Pecs, Hungary.

CHAPTER

17

CLAYS AS NEUTRALIZERS AGAINST ENVIRONMENTAL PROTECTION

A widespread recognition of the need to develop technologies for pollution control has arisen in only relatively recent times. This has been a result of increased awareness of the effects of pollution on the health and longevity of both human beings and the earth's fragile ecosystems. Therefore it is not surprising to find that clays were not used for environmental protection to any great extent until quite recently.

17.1 INTRODUCTION

To understand the role of clays in nature and their beneficial effects, it is important to have the preliminary knowledge about origin of clays and their transformation in nature.

In nature, generally three mechanisms are in operation for the formation of clays. They are: inheritance, neoformation and transformation.

Inheritance: Clay minerals remained in a natural deposit and originated from reactions that occurred in another area during a previous stage in the rock cycle. This type of clay is inert in nature. Its stability may result either from slow reaction rates or from being in chemical equilibrium. Clays that have inherited their crystal structure are indicators of their provenance.

Neoformation: In this case, clay is precipitated from solution or has been formed from reactions of amorphous material. These clays have precipitated in response to in situ conditions.

Transformation: Here clay is capable of preserving some of its relict inherited structure while undergoing chemical reaction. This reaction is of two types: (i) ion exchange, where loosely bound ions are exchanged with those of the

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environment, and (ii) layer transformation, where the arrangements of tightly bound octahedral, tetrahedral or fixed interlayered cations are relocated and reconstructed. The results of this type of transformation are better preserved in the geological record. Transformed clays moreover carry information of both inherited characters of source area and having reacted with in situ changes in the environment. Hence they are considered to have more implications than other types in assessing the role of clays in nature.

17.2 ORIGIN OF CLAYS

Clays and clay minerals occur under a fairly limited range of geologic conditions. The environments of formation include soil horizons, continental and marine sediments, geothermal fields, volcanic deposits and weathering rock formations. Most clay minerals form where rocks are in contact with water, air or steam. For example, weathering boulders on a hillside, sediments on sea or lake bottoms, deeply buried sediments containing pore water, and rocks in contact with water heated by magma. Extensive alteration of rocks to clay minerals can produce relatively pure clay deposits that are of economic interest.

Table 17.1: Various clay-forming processes

Process	*Illustrations*
Erosion	The transport and deposition of clays and clay minerals produced by eroding older continental and marine rocks and soils are important parts of the cycle that forms sedimentary rocks. The ancient sedimentary rock record is composed of about 70 percent mudstones (which contain about 50 percent clay-sized fragments) and shales (which are coarser than mudstones but which may contain clay-sized particles) (Blatt et al., 1980). Today, sedimentary environments that contain muds cover about 60 percent of marine continental shelves and 40 percent of deep ocean basins; continental aquatic environments such as lakes, rivers, estuaries and deltas also contain high proportions of fine-grained sediments (Hillier, 1995). Clearly, clays and clay minerals are critical components of both ancient and modern sedimentary environments.
Diagenesis	Diagenesis is the in-place alteration of a mineral to more stable forms, excluding surficial alteration (which is weathering); diagenesis occurs, for example, when minerals stable in one depositional environment are exposed to another by burial and compaction. Common silicate materials such as quartz, feldspar and volcanic glasses, as well as carbonates, noncrystalline iron oxides and primary clay minerals, are transformed during diagenesis into more stable clay minerals mainly by dissolution and recrystallization. The formation of bentonite (beds containing smectite-group clay minerals including montmorillonite) and Fuller's earth (a type of clay mineral deposit that has high capacity

(*Contd.*)

Table 17.1: (*Contd.*)

Process	*Illustrations*
	to absorb water) may occur primarily by diagenesis, although some deposits may also form by hydrothermal processes. Bentonite beds usually form from altered volcanic ash, but other types of rock may also serve as sources. The absorptive properties of bentonites and Fuller's earth make them ideal for such diverse uses as drilling mud; foundry-sand bond; binder for pelletizing iron ore and bleaching liquids; absorbents for oil, grease and animal waste; and carriers for pesticides and fertilizers. Bentonite is also used as a soil liner for environmental containment applications and with polyacrylamide for making paper.
Weathering	Weathering of rocks and soil is the primary way that clays and clay minerals form at the Earth's surface today. The weathering process involves physical disaggregation and chemical decomposition that change original minerals to clay minerals. Weathering is uneven, and many stages of breakdown may be found in the same clay sample. Factors governing rock weathering and soil formation include the initial type of rock, the ratio of water to rock, the temperature, the presence of organisms and organic material, and the amount of time. The types of clay minerals found in weathering rocks strongly control how the weathered rock behaves under various climatic conditions (such as humid-tropical, dry-tropical and temperate conditions). Kaolinite is found in most weathering zones and soil profiles. Montmorillonites, which are chemically more complex than kaolinites, are common in the lower parts of weathering profiles, nearer the rock, where chemistry exerts a strong control on mineralogy. Complex mixed-layer clay minerals (such as illite-smectites) are abundant in clay assemblages that develop from mica-bearing precursor rocks, such as the granite plutons that occur in temperate regions of the northeastern United States. For example, a large component of soils formed by weathering of granites may consist of metastable muscovite, biotite and chlorite. These minerals will alter progressively to clay minerals.

Mechanism **Environment**	**Inheritance**	**Neoformation**	**Layer transformation**
Sedimentary	Low energy Low temperature	Medium energy Low temperature	High energy Low temperature
Weathering	Low energy Medium temperature	Medium energy Medium temperature	High energy Medium temperature
Diagenetic-hydrothermal	Low energy High temperature	Medium energy High temperature	High energy High temperature

Fig. 17.1: Zonal variation of clay. (After Esquevin, 1958 and Millot, 1970)

On the basis of the ideas of Esquevin (1958) and Millot (1970), the mechanism of clay formation is divided into (i) inheritance, (ii) neoformation, and (iii) transformation. Origin by inheritance simply means that a clay mineral found in a natural deposit originated from reactions that occurred in another area during a previous stage in the rock cycle and that the clay is stable enough to remain inert in its present environment. Its stability may result either from slow reaction rates or from being in chemical equilibrium. Origin by neoformation means that the clay has precipitated from solution or has formed from reaction of amorphous material. Origin by transformation requires that the clay has kept some of its inherited structure intact while undergoing chemical reaction. This reaction may take two forms: (i) ion exchange, in which loosely bound ions are exchanged with those of the environment and (ii) layer transformation, in which the arrangements of tightly bound octahedral, tetrahedral or fixed interlayer cations are modified.

Clay's environment can be described in terms of temperature, pressure, chemical composition and reaction time. These variables are condensed into three geological situations based on the idea of Esquevin (1958) and Millot (1970): (i) the weathering environment, (ii) the sedimentary environment and (iii) the diagenetic-hydrothermal environment.

17.3 CLAY-ENVIRONMENT INTERACTION

- The potential effects of nonmarine clay-mineral alteration processes are of much greater consequence than are those in marine environments. In this case, they led to the formation of beds in which the clay-mineral suite is almost all kaolinite, whereas the gross qualitative detrital clay-mineral suite was little changed in marine waters.
- The actual extent and effect of the clay-mineral formation processes is quite variable, so that there is considerable overlap in clay-mineral composition between nonmarine and deltaic deposits.
- "Trace" clay-mineral constituents may be more sensitive environmental indicators than the gross clay-mineral composition, in this case presence or absence and crystallinity of the chlorite-vermiculite component was the most diagnostic parameter.

Table 17.2 gives some of the particular or proposed applications of clays for pollution control and environmental protection, delineates properties of clays that make them useful for these applications, and outlines the requirements for pre-treatment that enhance their effectiveness in each case.

17.4 CLAYS AND SOIL CHEMISTRY

The clay minerals, particularly expansible phases such as smectite and vermiculite, are very sensitive to the environment in which they occur. Because of the nature of the interlayer region, hydroxyl-interlayered vermiculite and

Table 17.2: Applications of clays for pollution control and environmental protection (Churchman et al., 2006)

Contaminants for control	*Status (actual or potential use)*	*Pretreatments required*	*Relevant clay properties*
Heavy metal cations and simple cations	Actual, mainly passive, use (e.g., in soils, liners)	Mostly none, some organic and inorganic modification	Charge, surface area, reactive surface groups
Organic and biological cations	Potential for water and wastewater treatment, pesticide control	Generally none, except cation saturation	Charge, surface area, especially interlayer
Non-ionic organic molecules	Actual, for water and wastewater treatment; potential, for pesticide control, waste liners	Cation saturation, organic or inorganic modification	Charge
Anions	Actual, for water and wastewater treatment; potential, for pesticide and nutrient leaching control	Appropriate organic modification	Charge
Turbidity and residual treatment chemicals	Actual, for treatment of potable water and some wastewaters and sewage	Generally none	Colloidal, from size and charge; charge, surface area
Leachates	Actual, for waste liners and radioactive waste storage	Generally none, except cation saturation	Swelling, charge, surface area, reactive surface groups

smectite are highly variable and changes in environmental conditions can be reflected in the degree of interlayer filling and in the relative stability of the interlayer components. Hence hydroxyl-interlayered clay phases in soils can be affected by changes in their environment caused by changes in land use and land management.

Many areas where there has been concern over acidification of surface waters from acid deposition from the atmosphere (so-called "acid rain") are those with podzolic soils in granitic terrain where the transformation of micas to vermiculite is one of the main mineral weathering processes (Wilson, 1986). Usually this process is manifested by the presence of interstratified mica-vermiculite with the interlayer space in the vermiculite often partially filled with polymeric hydroxyaluminium.

Case Study I

In a peaty podzol developed on quartz-mica-schist in Scotland, regularly interstratified mica-vermiculite was shown by Bain et al., 1990 to develop at the expense of mica and is the dominant mineral in the Eh horizon. This phase was concentrated by chemical treatments to remove organic matter and free iron oxides and both the mica and vermiculite components were shown to be dioctahedral in character. The amount of interstratified mica-vermiculite increased towards the surface in the soils studied with the result that there is more interlayer space available for adsorption on hydroxyaluminium in the upper horizons. The degree of interlayering as indicated by the degree of collapse of the vermiculite structure on heating was shown to be pH-dependent. Therefore the amount of hydroxyaluminium being leached down from the surface and which is adsorbed by the vermiculite appears to depend on the pH. Conversely, if the pH of a horizon should decrease, because of, say, acid precipitation, Al from the interlayer will be mobilized and may find its way into stream waters with potentially toxic consequences to fish. Hydroxyaluminium interlayered vermiculite may play a major role in the amounts of mobile Al^{3+} in catchments and variations in the clay mineral suites may play a key role in the chemical response and weathering processes occurring in catchments. Thus hydroxyaluminium interlayered swelling phases such as vermiculite and smectite could serve as good indicators of gradual changes in natural soil environments.

17.5 CLAYS AND LANDUSE PRACTICES

Velde and Peck (2002) investigated the clay mineralogy of soil samples and showed that there is a significant influence of the cropping method on the clay minerals in the soils. X-ray diffraction curve decomposition methods were used to identify and follow the evolution of the different clay minerals: mica, illite and two randomly mixed-layered illite-smectite phases. Velde and Peck also proposed that the illite-smectite minerals play the role of a potassium-buffer, becoming K-poor when the soil cannot furnish enough K from mineral reserves of detrital phases and K-rich when the soil is able to release enough K to enter into the illite-smectite minerals, where it is available during a growing season, for plant growth. This work shows that crops can affect the clay mineralogy of the soils on which they are grown over periods of time relevant to modern agriculture and that there can be a significant influence of cropping method on soil clays over 80 years.

Case Study II

Flood irrigation was found to cause a rather rapid irreversible transformation of soil clay minerals and loss of potassic minerals (in 30 years or less) despite the use of fertilizers.

The clay minerals in flood-irrigated Chinese paddies are studied by Li et al. (2003). Three clay minerals were found to be initially present in these soils: illite-mica, magnesium chlorite and an interstratified mica-aluminous chlorite. The K-bearing phases (discrete mica and illite as well as interstratified mica layers) are to a large extent lost while the Fe content decreases in the soil as a whole and increases in the chlorite. The mica component in the mixed-layer mineral also decreases. Li et al. (2003) concluded that these changes in clay mineralogy and relative abundance suggest a loss of potassic minerals and an increase in the formation of less siliceous, more ferromagnesian chlorite.

Case Study III

Bain and Griffen (2002) studied three Scottish soil profiles adjacent to each other and developed on similar schistose parent material but under different land use. The profile under 50-year old Sitka spruce trees was the most acidic; the second profile under rough grassland was less acidic and the third profile in an arable field which had been fertilized was the least acidic. The clay fractions of all three profiles are similar. However, computer simulations of the X-ray diffraction patterns of the clay phases using a modified version of NEWMOD revealed two possible weathering trends:

1. An increasing proportion of vermiculite in interstratified mica-vermiculite in the upper horizons of the arable and forested soils due to weathering of mica by loss of interlayer potassium.
2. Formation of high-charge corrensite by weathering of chlorite in all three profiles but least pronounced in the arable soil.

The differences in clay mineralogy amongst the profiles are minor, but these two different weathering trends may be due to the effects of different land use.

17.6 APPLICATION OF CLAYS FOR REMOVAL OF POLLUTANT IONS

17.6.1 Heavy Metal Cations

As cation exchangers, clays are effective for the control of cations in solution, although, in case of ion exchange only, their effectiveness is governed by the attaining equilibrium between ions in solution and those on exchange sites. However, clays are most useful for the control of cationic pollutants when the mechanism of uptake extends beyond that of just cation exchange. In waste repositories clays are used as liners for the control of heavy metal ions, often among other pollutants. Otherwise, clay minerals in soils, along with metal hydr(oxides) and organic matter, control the concentrations of heavy metal ions in surrounding and leaching solutions.

The preference of bentonites for heavy metal ions that adsorb by cation exchange decreases in the order $Cu^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+} > Mn^{2+}$ (Lagaly, 1995). According to Lagaly, the selectivity of montmorillonite for cations generally depends on the restriction of interlayer expansion, being minimal for sodium montmorillonites. Metwally et al. (1993) found palygorskite to be more effective than montmorillonite, and very much more effective than kaolinite, for the uptake of Zn^{2+}, at least under the conditions of their experiments (pH 4.5–7.0). Minerals were tailored to remove particular elements (e.g., radioactive species) quite specifically. By this means high affinities for Cu^{2+} and Pb^{2+} (Kodama and Komarneni, 1999), Sr^{2+} (of importance as 90Sr in radioactive wastes) (Komarneni et al., 2000), and radium ions (Komarneni et al., 2001) were obtained with Na^{+}-rich micas synthesised from kaolinite. Some natural clay can also show a high selectivity for particular cations, e.g., palygorskite (attapulgite) for radioactive Cs^{+} (Chandra, 1970).

Table 17.3: Uptake of heavy metal cations by clay minerals and their derivatives

Minerals	*Uptake mechanisms*
Bentonite	• The immobilisation of small cations (e.g., Cr^{3+}) on bentonite surfaces requires less heating (lower temperatures) as compared with the larger-adsorbed cations (Pb^{2+}, Cd^{2+}, Ni^{2+}). • Zinc ions adsorbed by dimethyl dioctadecylammonium (DMDOA) bentonite is virtually trebled in the presence of phenol and diethyl ketone. • Lead and chlorobenzene are adsorbed simultaneously by a bentonite that has been modified with hexadecyltrimethylammoniu (HDTMA) (Lee et al., 2002).
Montmorillonite	• Formation of complex compounds with cysteine aids the uptake of Cd^{2+} (Undabeytia et al., 1998). • Poly(hydroxo iron) or poly(hydroxo iron/aluminium)-interlayered montmorillonites have higher affinities for Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} than the corresponding poly (hydroxo aluminium) compounds (Cooper et al., 2002).
Kaolinite	• Cd^{2+}-cysteine can intercalate into kaolinite to some extent, and more so into a less well-ordered than a well-ordered kaolinite. • For the clean-up of galvanic water, grafting polyphosphates on to the edges of kaolinite, metakaolinite, and Al^{3+} (hydr)oxides greatly increases the capacities of these materials to remove Ni^{2+}, Co^{2+} and Cr^{3+} from solutions through the formation of complexes with the phosphate groups (Tarasevich and Klimova, 2001).
Smectite	• Modification of smectites by interlayering with hydroxy-cations and pillaring can markedly increase the uptake of heavy metal cations, especially certain specific metal ions. • In studying the adsorption of Cu^{2+} on a poly(hydroxo aluminium) interlayered smectite between pH 4.5 and 6.5, this adsorbent is much more reactive towards Cu^{2+} than either montmorillonite itself or aluminium (hydr)oxides (Harsh and Doner, 1984).

17.6.2 Organic and Biological Cations

Clay minerals are mostly negatively charged; so they pose a strong affinity for organic cations. Although the number of organic species that can acquire a positive charge or act as a base may be limited (Theng, 1974), some of these are important. For example, the pesticides paraquat and diquat create problems as pollutants whereas amines, especially alkylammonium cations, are useful for modifying clay properties, and amino acids, peptides and proteins are biologically important. In following ways clay minerals can be used to control pollution, caused by organic cations:

- Bentonite used to constrain the leakages in plastic storage drums, draining paraquat and diquat (Stansfield, 1986).
- Fine-grained marine sediment, containing kaolinite and montmorillonite, was able to adsorb mycrocystin-LR, indicateing the potential use of clays to remove this class of potent mammalian liver toxins from drinking waters (Morris et al., 2000).
- Some bentonites can remove all the proteins from abattoir wastes which otherwise could cause eutrophication of aqueous systems (Churchman, 2002).
- The ability of clay minerals to adsorb viruses (nucleoproteins) in a similar way to proteins (Theng, 1979) can be put to various beneficial uses as well.

17.7 ROLE OF CLAY TO REDUCE ORGANIC POLLUTANTS

Because of their charge characteristics, clays are naturally hydrophilic. Nevertheless, their high-surface areas and volume of fine pores enable them to adsorb significant amount of non-ionic substances. There are records of the use of clays for 'fulling', i.e., cleaning grease from wool, that date back before 2000 BC; hence the term 'fuller's earth' (Robertson, 1986). Fuller's earth generally denotes calcium montmorillonite, although it is sometimes used to refer to palygorskite (attapulgite), especially in the USA. Today, clays are used quite widely to adsorb oil and grease, e.g. on floors of workshops (Grim, 1962). Coarser particles are preferred for this purpose, and palygorskite is particularly suitable, while montmorillonite that has been calcined to a sufficiently high temperature to prevent its break-up into small particles is also used. However, clays in their natural state usually effect little uptake of small non-ionic organic compounds (NOCs) in the presence of water. Despite this drawback, their attractiveness for environmental applications as low-cost, generally non-toxic, high surface-area materials mean that much recent research has gone into the adaptation of clays for the removal of NOCs, which include many substances of concern to environmental and human health.

While most research on the modification of clay minerals for non-ionic organic contaminant uptake has been carried out on smectites, some has shown the feasibility of this approach for a wide range of clay minerals. Indeed, the enhanced uptake of a number of NOCs by soils containing many different clay minerals besides smectites (Boyd et al., 1988a, 1988b) suggested the universal applicability of this approach for clay minerals. A study of uptake of a range of hydrocarbons by the hexadecyltrimethylammonium (HDTMA) derivatives of a variety of clay minerals (Jaynes and Boyd, 1991a) has confirmed the effectiveness of these organo-clays as adsorbents of hydrocarbons. A vermiculite, a high-charge smectite, and an illite each retained more ethylbenzene than a low-charge smectite and a kaolinite. In following ways clay minerals can be used to control pollution, caused by non-ionic organic compounds:

- The organo-clays (McBride and Mortland, 1973; Kokai, 1975; Beall, 1984, 1985a, 1985b, 1996; Alther, 1999) were used most widely for removing oil and grease from water. They are included in a patent for the specialised task of clearing spills of oil on water (Kemnetz and Cody, 1996).
- They are used for the removal of mycrocystin toxins from cyanobacteria (blue-green algae) that accumulate in waterways and water storages (Gates and Slades, 2001).
- They may also be used to remove waste organic materials from industrial processes, such as tanneries (Cioffi et al., 2001).
- Organo-clays were also proposed for use in waste containment barriers (Smith et al., 1990; Sheng et al., 1996a, 1996b). Modelling has shown that small amounts of these materials included in conventional clay barriers would enable effective containment of NOCs for >100 years (Adu-Wusu et al., 1997).
- Organo-clays may also be used as adsorption (chemical) barriers in association with landfill liners, where they can increase the useful life of the associated liner by 5–10 years (Voudrias, 2002).
- They can also be employed as containment barriers for BTEX pollutants around petroleum storage tanks (Jaynes and Vance, 1996; Xu et al., 1997; Sharmasarkar et al., 2000; Lo and Yang, 2001).
- Since clays are ubiquitous components of soils and many other earth materials (e.g., sediments and regolith), the knowledge gained from research on organo-clays has found application in the in situ modification of soils for taking-up and immobilizing NOCs. Particular uses to which this technology can be put include the immobilisation of leachable pollutants in contaminated land (Boyd et al., 1988a, 1988b; Lee et al., 1989; Brixie and Boyd, 1994; Xu et al., 1997). This approach can prevent the transport by leaching of pesticides into ground water. To this end, soils, subsoils and aquifer materials are treated with QACs to provide adsorptive zones for the retardation of pesticide transport (Sheng and Boyd, 1998).

17.8 ROLE OF PYROPHYLLITE CLAY AS NEUTRALIZER

Pyrophyllite clay is known to contain approximately 60% silica of which about 85% is non-crystalline, round amorphous silica molecules. This amorphous construction gives the clay particles an exceptional amount of free surface area to attract and hold toxic compounds, and offer its nutrients to the soil and plants. Silica-rich naturally cleans up polluted land as it increases mineral content within the soil and builds nutrients within the plant. Silica-rich pyrophyllite clay holds the potential of being an ideal soil amendment. With phosphate-poisoned soils producing lesser yields and lower quality crops, the trend is moving toward a return to organic. Organically farmed acreage in America is currently doubling in size every five years. As demonstrated in the following field tests, pyrophyllite clay holds the answer to cleaning up toxic soils, replacing lost nutrients in the soil, and quickly restoring the land to organic status.

Field Tests Prove Pyrophyllite Superior to Triple Phosphate Fertilizers
A group of field tests began in 1856 using three comparison groups—sodium silicates, triple phosphates and a control group. The tests were performed at Rothhamsted Experiment Station, Rothhamsted, England. These tests showed that silica in an amorphous state caused more phosphate to be made available for plants than adding triple phosphate fertilizers to the soil. The amorphous silica accomplished this feat, in part, by releasing the locked up phosphates already existing in the soil from previous years of phosphate use. These tests continued every year until 1950 with the same results. About a 5% greater increase in crop yield were observed in the silica fertilized plots than the plots treated with triple phosphates. This increase in yield was accomplished without additional phosphate. With the aid of Dr. E. Epstein of UC Davis, the University of Florida did tests using amorphous silica to combat the leaching of phosphates into Lake Okeechobee. These tests were completed and a final report showing the results was published in 1999. The tests show that when amorphous silica is applied to soils, it has the ability to unlock phosphates making them available for plant use. At the same time, the silica produced an increase in minerals and other nutrients within the plants, resulting in healthier, more disease-resistant produce. The side benefit of this conversion of phosphates in favour of the plant was a reduction of phosphate runoff into Lake Okeechobee.

Another important side effect was discovered through this testing. The application of amorphous silica actually helped to clean up the environment by adsorbing heavy metals, pesticides, and insecticides. (In the US many cities have banned phosphate use within their city limits due to the ecological damage phosphate fertilizers have caused to the land and water supplies through phosphate runoff.) The results of these tests indicate that pyrophyllite clay has great promise in the agricultural industry as a silicon soil amendment and soil detoxifier.

Pyrophyllite clay is known to possess a weak van der Waals bond giving it the property of dispersing easily in water. This property is highly desirable for a clay, since it is this property that keeps the clay from clumping. This dispersing property allows for greater surface exposure of the clay in the soil, therefore more toxins are able to be contacted and absorbed. Clumping clay like bentonite can be less effective than dispersing clay due to its more limited exposure of its surface area to toxins. With pyrophyllite clay being easily dissolved in water without clumping, a greater surface area of the clay is made available to the land for detoxifying purposes. With the clay possessing both absorbing (like a sponge) and adsorbing (like a magnet) properties, its detoxifying properties are exceptionally high.

From an environmental perspective, silica-rich pyrophyllite clay may well provide us with a means to clean up much of the pollution in the land, the waterways and possibly in the ocean. When the world's phosphate reserves are nearly depleted, silica-rich pyrophyllite clay is becoming known as the ideal replacement to help clean up the soils from the damage done by phosphate fertilizers, and to restore the soil (and perhaps our bodies) back to their original healthy, organic state.

Concluding Remarks

The use and utilization of clays for the control of each of the different classes of pollutants has reached its own particular stage of development. With passage of time new targets for the environmental use of clays and also for overcoming some of the problems raised in their environmental applications to date are in the process to be reached.

QUESTIONS

1. Illustrate the role of clays as neutralizers.
2. State why the clays formed by transformation are considered to have more implications than other types in assessing the role of clays in nature.
3. Citing the phenomenon of clay-environment interaction, comment on the role of clays in neutralizing pollution.
4. Individually depict the roles of smectite and vermiculite explaining their properties in maintaining ecological balance.
5. How clays can neutralize the effect of pollution via landuse practices?
6. 'The preference of bentonites for heavy metal ions that adsorb by cation exchange decreases in the order $Cu^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+} > Mn^{2+}$.' How this can be employed in reducing pollution activities?
7. How do clay minerals react with organic cations to prevent pollution?
8. Define organo-clays. Illustrate briefly their role in combating pollution.

FURTHER READING

Adu-Wusu, K., Whang, J.M. and McDevitt, M.F. (1997). Modification of clay-based waste containment materials. *Land Contamination & Reclamation*, **5:** 171–175.

Bain, D.C. and Griffen, D.T. (2002). Possible effects of land use on the clay mineralogy of a brown forest soil. *Clay Minerals*, **37:** 663–670.

Bain, D.C., Mellor, A. and Wilson, M.J. (1990). Nature and origin of an aluminous vermiculitic weathering product in acid soils from upland catchments in Scotland. *Clay Minerals*, **25:** 467–475.

Beall, G.W. (1984). Method of breaking emulsions; absorption of a quaternary ammonium exchanged clay in wastewater. U.S. Patent 4,470,912.

Beall, G.W. (1985a). Process for treating organic contaminated water; organoclay absorption column followed by active carbon. U.S. Patent 4,517,094.

Beall, G.W. (1985b). Method of removing organic contaminants from aqueous compositions; absorption with reaction product of clay and quaternary ammonium salt. U.S. Patent 4,549,590.

Blatt, H., Middleton, G. and Murray, R. (1980). Origin of sedimentary rocks (2nd ed.). Prentice-Hall, Englewood Cliffs, N.J., 766 p.

Boyd, S.A., Lee, J.F. and Mortland, M.M. (1988a). Attenuating organic contaminant mobility by soil modification. *Nature*, **333:** 345–347.

Boyd, S.A., Mortland, M.M. and Chiou, C.T. (1988b). Sorption characteristics of organic compounds on hexadecyltrimethylammonium-smectite. *Soil Science Society of America Journal*, **52:** 652–657.

Brixie, J.M. and Boyd, S.A. (1994). Treatment of contaminated soils with organoclays to reduce leachable pentachlorophenol. *Journal of Environmental Quality*, **23:** 1283–1290.

Chandra, U. (1970). Removal of radioisotopes from liquid wastes by sorption in local minerals. NTIS. BARC-454, 29pp. (Water Resources Abstract No. 7109517).

Churchman, G.J. (2002). Formation of complexes between bentonite and different cationic polyelectrolytes and their use as sorbents for non-ionic and anionic pollutants. *Applied Clay Science*, **21:** 177–189.

Churchman, G.J., Gates, W.P., Theng, B.K.G. and Yuan, G. (2006). Clays and clay minerals for pollution control. *In:* Handbook of Clay Science. F. Bergaya, B.K.G. Theng and G. Lagaly (eds). Developments in Clay Science, **1:** 625–676.

Cioffi, R., Costanzo, S., Maffucci, L. and Santoro, L. (2001a). Adsorption of the organic fraction of a tannery sludge by means of organophilic bentonite. *Environmental Technology*, **22:** 83–89.

Eberl, D.D. (1984). Clay mineral formation and transformation in rocks and soils. *Phil. Trans. R. Soc. Lond.*, **A311:** 241–257.

Gates, W.P. and Slade, P.G. (2001). Removal of toxins from water. Australian Patent No. PCT/ AU01/00586.

Grim, R.E. (1962). Applied Clay Mineralogy. McGraw-Hill, New York.

Hillier, S. (1995). Erosion, sedimentation and sedimentary origin of clays. *In:* Velde, B. (ed.). Origin and mineralogy of clays. Springer-Verlag, New York.

Jaynes, W.F. and Vance, G.F. (1996). BTEX sorption by organo-clays: cosorptive enhancement and equivalence of interlayer complexes. *Soil Science Society of America Journal*, **60:** 1742–1749.

Kemnetz, S. and Cody, C.A. (1996). Oil spill flocculating agent and method of remediating oil spills. U.S. Patent 5,558,777.

Kokai, T. (1975). Japanese Patent Application. **25:** 489.

Komarneni, S., Kodama, T., Paulus, W.J. and Carlson, C. (2000). Synthetic clay excels in Sr-90 removal. *Journal of Materials Research*, **15:** 1254–1256.

Komarneni, S., Kozai, N. and Paulus, W.J. (2001). Superselective clay for radium uptake. *Nature*, **410:** 771.

Lagaly, G. (1995). Surface and interlayer reactions: bentonites as adsorbents. *In:* Churchman, G.J., Fitzpatrick, R.W., Eggleton, R.A. (eds). Clays: Controlling the Environment. Proceedings of the 10th International Clay Conference. Adelaide, Australia, 1993. CSIRO Publishing, Melbourne.

Lee, J.F., Crum, J.R. and Boyd, S.A. (1989b). Enhanced retention of organic contaminants by soils exchanged with organic cations. *Environmental Science and Technology*, **23:** 1365–1372.

Li, Z., Velde, B. and Li, D. (2003). Loss of K-bearing clay minerals in flood-irrigated, rice-growing soils in Jiangxi Province, China. *Clays and Clay Minerals*, **51:** 75–82.

Lo, I.M.C. and Yang, X.Y. (2001). Laboratory investigation of the migration of hydrocarbons in organobentonite. *Environmental Science and Technology*, **35:** 620–625.

McBride, M.B. and Mortland, M.M. (1973). Segregation and exchange properties of alkylammonium ions in a smectite and vermiculite. *Clays and Clay Minerals*, **21:** 323–329.

Millot, G. (1970). Geology of clays. Springer-verlag, New York.

Morris, R.J., Williams, D.E., Luu, H.A., Holmes, C.F.B., Andersen, R.J. and Calvert, S.E. (2000). The adsorption of mycrocystin-LR by natural clay particles. *Toxicon*, **38:** 303–308.

Metwally, A.I., Mashhady, A.S., Falatah, A.M. and Reda, M. (1993). Effect of pH on zinc adsorption and solubility in suspensions of different clays and soils. *Zeitschrift fu¨r Pflanzenerna¨hrung und Bodenkunde*, **156:** 131–135.

Robertson, R.H.S. (1986). Fuller's Earth: A History of Calcium Montmorillonite. Volturna Press, Hythe, Kent.

Sharmasarkar, S., Jaynes, W.F. and Vance, G.F. (2000). BTEX sorption by montmorillonite organo-clays: TMPA, ADAM, HDTMA. *Water, Air and Soil Pollution*, **119:** 257–273.

Sheng, G.Y. and Boyd, S.A. (1998). Relation of water and neutral organic compounds in the interlayers of mixed Ca/trimethylphenylammonium-smectites. *Clays and Clay Minerals*, **46:** 10–17.

Sheng, G.Y., Xu, S.H. and Boyd, S.A. (1996a). Cosorption of organic contaminants from water by hexadecyltrimethylammonium-exchanged clays. *Water Research*, **30:** 1483–1489.

Sheng, G.Y., Xu, S.H. and Boyd, S.A. (1996b). Mechanism(s) controlling sorption of neutral organic contaminants by surfactant-derived and natural organic matter. *Environmental Science and Technolology*, **30:** 1553–1557.

Smith, J.A., Jaffe´, P.R. and Chiou, C.T. (1990). Effect of ten quaternary ammonium cations on tetrachloromethane sorption to clay from water. *Environmental Science and Technolology*, **24:** 1167–1172.

Stansfield, R.A. (1986). The diquat incident at Woodkirk, Yorkshire. *European Water and Sewage*, **90:** 450–451.

Theng, B.K.G. (1974). The Chemistry of Clay-Organic Reactions. Adam Hilger, London.

Theng, B.K.G. (1979). Formation and Properties of Clay–Polymer Complexes. Elsevier, Amsterdam.

Velde, B.Y. and Peck, T. (2002). Clay mineral changes in the Morrow experimental plots. University of Illinois. *Clays and Clay Minerals,* **50:** 364–370.

Voudrias, E.A. (2002). The concept of a sorption chemical barrier for improving effectiveness of landfill liners. *Waste Management and Research*, **20:** 251–258.

Wilson, M.J. (1986). Mineral weathering processes in podzolic soils on granitic materials and their implications for surface water acidification. *Journal of the Geological Society of London*, **143:** 691–697.

Xu, S., Sheng, G.Y. and Boyd, S.A. (1997). Use of organoclays in pollution abatement. *Advances in Agronomy*, **59:** 25–62.

CHAPTER

18

ENVIRONMENTAL DEGRADATIONS DURING CLAY MINING AND BENEFICIATION

Clays and clay minerals have been mined since the Stone Age; today they are among the most important minerals used by manufacturing and environmental industries. Hence it is necessary to have a profound knowledge about the environmental degradations, taking place during clay mining and beneficiation. In turn it will pave the way to innovate the processes by which these degradations can be reduced, thereby removed.

18.1 INTRODUCTION

Clay is defined as a natural, earthy, fine-grained material, largely of a group of crystalline hydrous silicate minerals known as clay minerals. The usual types of mines are open pit but underground mining is also done for clay, associated with coal deposits and more profitable, particularly for fire clays.

The environmental disturbance is created to the land through open pit or cut-and-fill mining. A depression or pit is created when the overburden and the clays are removed. State laws usually require levelling or contouring of the disturbed area and planting trees or grasses to prevent or minimize erosion. Ponds for recreational purposes often are created when groundwater levels permit. For processing, the impoundment of slimes and dust control is required. The rules for disposal of coarse tailings are similar to or included within those laws governing reclamation of the mined area.

18.2 CLAY MINING AND BENEFICIATION

Six types of clays are generally mined: ball clay, bentonite, vermiculite, common clay and shale, fire clay, Fuller's earth, and kaolin. Most domestic clays are

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mined by open-pit methods using various types of equipment, including draglines, power shovels, front-end loaders, backhoes, scraper-loaders, and shale planers. In addition, some kaolin is extracted by hydraulic mining and dredging. Most underground clay mines are located in Pennsylvania, Ohio and West Virginia, where the clays are associated with coal deposits. A higher percentage of fire clay is mined underground than other clays, because the higher quality fire clay deposits are found at depths that make open-pit mining less profitable. Clays usually are transported by trucks from the mine to the processing plants, many of which are located at or near the mine. For most applications, clays are processed by mechanical methods, such as crushing, grinding and screening that do not appreciably alter the chemical or mineralogical properties of the material. However, because clays are used in such a wide range of applications, it is often necessary to use other mechanical and chemical processes, such as drying, calcining, bleaching, blunging and extruding to prepare the material for use. Primary crushing reduces material size from as much as one metre to a few centimetres in diameter and typically is accomplished using jaw or gyratory crushers. Rotating pan crushers, cone crushers, smooth roll crushers, toothed roll crushers and hammer mills are used for secondary crushing, which further reduces particle size to 3 mm (0.1 in.) or less. For some applications, tertiary size reduction is necessary and is accomplished by means of ball, rod or pebble mills, which are often combined with air separators. Screening typically is carried out by means of two or more multi-deck sloping screens that are mechanically or electromagnetically vibrated. Pug mills are used for blunging, and rotary, fluid bed and vibrating grate dryers are used for drying clay materials. At most plants the calcine clay, rotary or flash calciners are used. However, multiple hearth furnaces often are used to calcine kaolin.

For the different types of clays, mentioned above, the mining methods and source areas have been discussed here to get a clear picture of their subsequent effect on environment.

Bentonite

Bentonite and Fuller's earth are mined worldwide. The USA is the major producer of bentonite and Fuller's earth. Approximately 90% of world bentonite production is concentrated in 13 countries: the USA, Greece, the Commonwealth of Independent States, Turkey, Germany, Italy, Japan, Mexico, Ukraine, Bulgaria, Czech Republic, South Africa and Australia. In addition to the mining of natural deposits, small amounts of bentonite, mainly hectorite, are produced synthetically in both Europe and the USA for use as a catalyst.

Most bentonite is mined by stripping methods from open pits after removing any overburden, although underground methods are used in a few places, such as the Combe Hay district in the United Kingdom (Patterson and Murray, 1983). Since deposits are often not uniform in composition, bentonite from a single pit may be separated into several stockpiles, which subsequently are blended to obtain the desired composition. Bentonite is usually processed by breaking large pieces into smaller fragments, drying at low to moderate temperatures to remove water and other volatiles without altering the molecular structure of the bentonite, and grinding to the desired size. The desired size is generally 200 mesh (US standard sieve size) or finer, which is equivalent to particle diameters of less than 70 µm. A coarser granular material is also produced for kitty litter applications. Processing may also include beneficiation, which may involve removing sand and other impurities as well as modifying the type of exchangeable ions in the crystal lattice. Some of the calcium bentonite produced in Texas, USA, is, for example, treated with sodium hydroxide to replace calcium with sodium in the montmorillonite and make the resulting product more suitable for use in drilling mud (Hosterman and Patterson, 1992). An organic-clad bentonite is produced for speciality purposes (paint, speciality greases, etc.) by replacing the inorganic exchangeable cations in the montmorillonite with an alkyl ammonium organic cation and is marketed under trade names such as Bentone and Nikkagel.

A flow diagram for bentonite processing is provided in Fig. 18.1. Mined bentonite first is transported to the processing plant and stockpiled. If the raw clay has a relatively high moisture content (30 to 35 per cent), the stockpiled material may be plowed to facilitate air drying to a moisture content of 16 to 18 per cent. Stockpiled bentonite may also be blended with other grades of bentonite to produce a uniform material. The material then is passed through a grizzly and crusher to reduce the clay pieces to less than 2.5 cm (1 in.) in size. Next, the crushed bentonite is dried in rotary or fluid bed dryers fired with natural gas, oil or coal to reduce the moisture content to 7 to 8 per cent. The temperatures in bentonite dryers generally range from 900°C (1650°F) at the inlet to 100 to 200°C (210 to 390°F) at the outlet. The dried material then is ground by means of roller or hammer mills. At some facilities which produce specialized bentonite products, the material is passed through an air classifier after being ground. Soda ash also may be added to the processed material to improve the swelling properties of the clay.

Fuller's Earth

A flow diagram for Fuller's earth processing is provided in Fig. 18.2. After being mined, Fuller's earth is transported to the processing plant, crushed, ground, and stockpiled. Before drying, Fuller's earth is fed into secondary grinders to reduce further the size of the material. At some plants, the crushed material is fed into a pug mill, mixed with water, and extruded to improve the properties needed for certain end products. The material then is dried in rotary or fluid bed dryers fired with natural gas or fuel oil. Drying reduces the moisture content to 0-10 per cent from its initial moisture content of 40-50 per cent. The temperatures in Fuller's earth dryers depend on the end uses of the product. For colloidal grades of Fuller's earth, drying temperatures of approximately 150°C (300°F) are used, and for absorbent grades, drying temperatures of 650°C

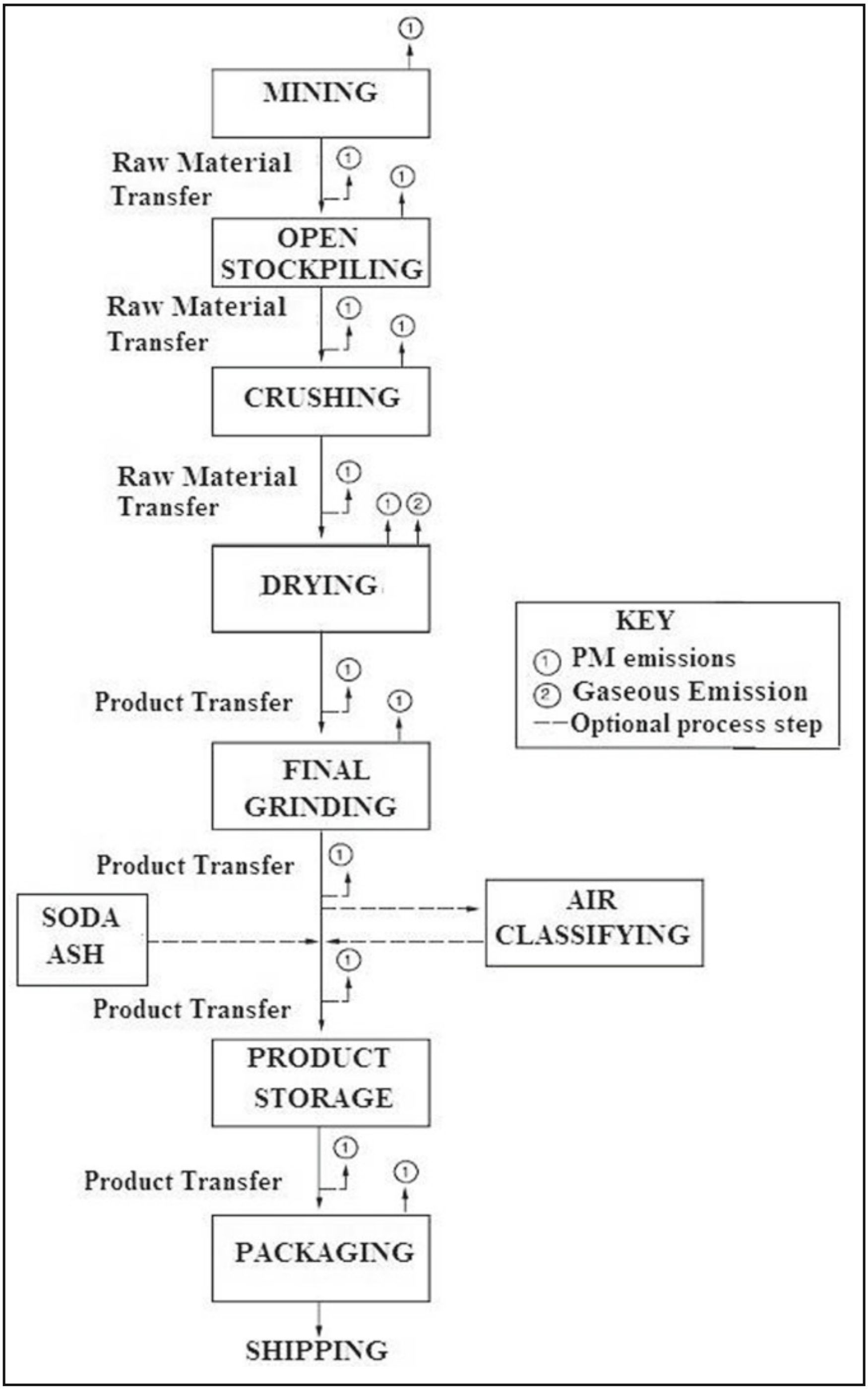

Fig. 18.1: Process flow diagram for bentonite processing (SCC = Source Classification Code).

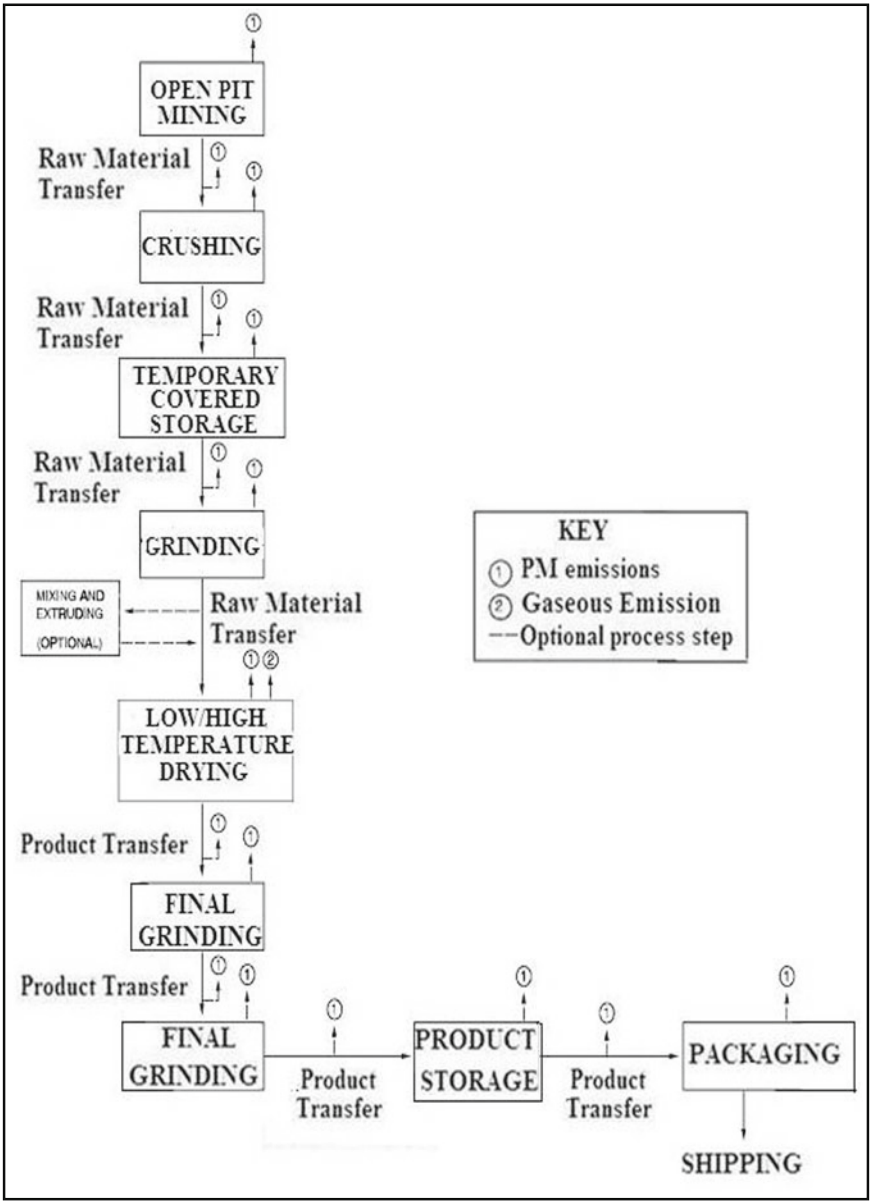

Fig. 18.2: Process flow diagram for Fuller's earth processing (SCC = Source Classification Code).

(1200°F) are typical. In some plants, Fuller's earth is calcined rather than dried. In these cases, an operating temperature of approximately 675°C (1250°F) is used. The dried or calcined material then is ground by roller or hammer mills and screened.

Kaolin

Large quantities of kaolin are mined and traded internationally. Virta (2002) lists 55 countries with a production of more than 1000 tonnes per year. The People's Republic of China was estimated to produce 1.9, 2 and 2.12 million tonnes in 2000, 2001 and 2002 respectively (Lines, 2003). The estimated annual production capacity of kaolin in China was 3.2–3.4 million tonnes in 2002–2003, out of which washed kaolin was only 700,000 tonnes (Ma and Tang, 2002; Moore, 2003).

Kaolin is both dry- and wet-processed. The dry process is simpler and produces a lower quality product than the wet process. Dry-processed kaolin is used mainly in the rubber industry, and to a lesser extent, for paper filling and to produce fibreglass and sanitary ware. Wet-processed kaolin is used extensively in the paper manufacturing industry. A process flow diagram for kaolin mining and dry processing is presented in Fig. 18.3 and Fig. 18.4 illustrates the wet processing of kaolin.

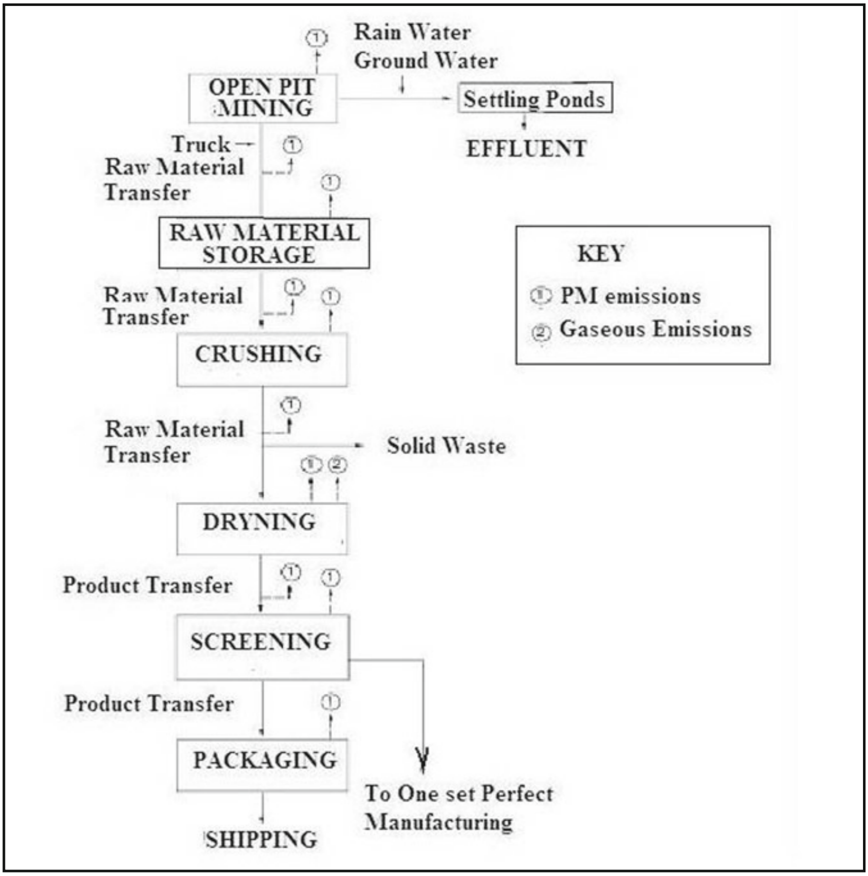

Fig. 18.3: Process flow diagram for kaolin mining and dry processing (SCC = Source Classification Code).

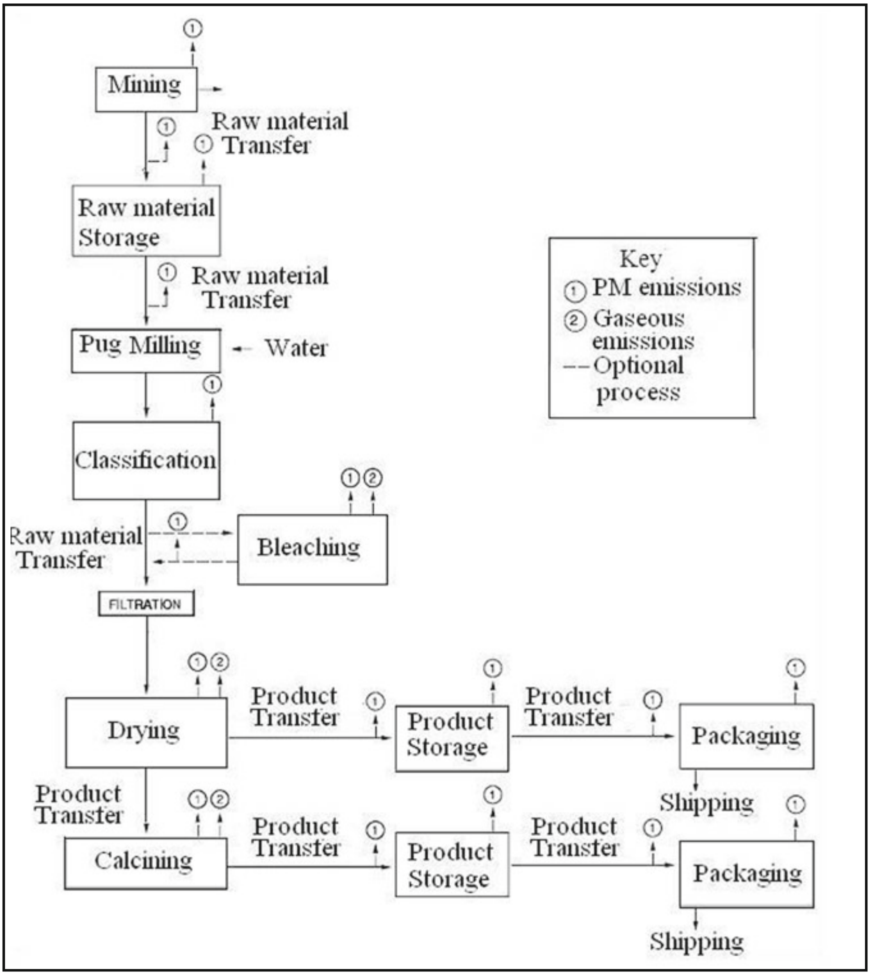

Fig. 18.4: Process flow diagram for wet process kaolin for high grade products (SCC = Source Classification Code).

In the dry process, the raw material is crushed to the desired size, dried in rotary dryers, pulverized and air-floated to remove most of the coarse grit. Wet processing of kaolin begins with blunging to produce slurry, which then is fractionated into coarse and fine fractions using centrifuges, hydrocyclones, or hydroseparators. At this step in the process, various chemical methods, such as bleaching, and physical and magnetic methods, may be used to refine the material. Chemical processing includes leaching with sulphuric acid, followed by the addition of a strong reducing agent such as hydrosulphite. Before drying, the slurry is filtered and dewatered by means of a filter press, centrifuge, rotary vacuum filter, or tube filter. The filtered dewatered slurry material may be shipped or further processed by drying in apron, rotary, or spray dryers. Following the drying step, the kaolin may be calcined for use as filler or refractory material. Multiple hearth furnaces are most often used to calcine kaolin. Flash and rotary calciners also are used.

Kaolin is usually removed from the mines in large moist lumps, and the initial process of refining involves chiefly a change in the physical state. Two main methods have been used for the refining of the natural clay: the air flotation or dry process, and the wet process. In the dry process, the clay is dried, pulverized, and then carried by currents of hot air into classifying chambers, from which it emerges as a stream of finely powdered kaolin. This process, which generates huge amounts of dust, was generally used prior to 1940 and has now been largely replaced by the wet process. In this process, the crude clay is mixed with water and vigorously agitated, and the individual kaolin particles are thus separated from each other and suspended in water. Water is then removed using different procedures (Edenfield, 1960).

Because of the varying composition of raw kaolin and different uses, raw kaolin generally requires processing (flotation, sedimentation, baking, etc.) to acquire characteristics suited to specific industrial uses.

Illite

Illite is often an important or dominant component of common clay (Murray, 1994). Common clay is produced worldwide and is a major industrial mineral. In the USA, common clay and shale are produced in 41 states. In 2002, this production was 23 million tonnes and had a value of $148 million (Virta, 2002). Illite occurs in commercially valuable purity and quantity in Malaysia (Bidor area of Perak), the USA (Illinois), the United Kingdom (South Wales), and Hungary (Tokaj Mountain in the north-eastern part of the country) (Grim, 1968; Fan and Aw, 1989). The most valuable ore is pure white and contains minimal iron. The commercial utility and thus the value of illite deposits may be reduced by lack of homogeneity in mineral content. There is no information on the annual production of relatively pure illite worldwide or by country.

18.3 ENVIRONMENTAL DEGRADATIONS

Environmental degradations include both natural pollution and biodegradations.

Pollution

Unlike other industrial sectors, mining activities particularly opencast mines, draw special attention from environmental degradation point of view. Besides air and water pollutions, it involves excavations of land, loss of soil, degradation/disfiguring of surface area and deforestation. Valuable topsoil and usable land is lost forever, which cannot be fully recovered. Natural drainage system and groundwater table is disturbed which not only affects the inhabitants in close proximity but also people living in faraway places.

Thus, clay mining also has an environmental impact because of the disturbance to the land through open pit or cut-and-fill mining methods.

Land degradation and surface distortions due to mining activity is not taken very seriously. Besides the active mining area, surrounding areas are also affected due to changes in surface drainage pattern, washouts and new gullies formed, which disturb the land use pattern. Loss of topsoil in the process from extensive areas is a great loss. Even the measures taken for reclamation, rehabilitation and aforestations cannot bring back normalcy for sustaining the local habitat. The new forests do not have branches, fruits and flowers to attract the fauna. Adequate monitoring, research and attention are required in this front, as it may differ from zone to zone.

The primary pollutants of concern in clay processing operations are particulate matter (PM) and PM less than 10 micrometres (PM-10). Particulate matter is emitted from all dry mechanical processes, such as crushing, screening, grinding, and materials handling and transfer operations. The emissions from dryers and calciners include products of combustion, such as carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x), and sulphur oxides (SO_x), in addition to filterable and condensable PM. Volatile organic compounds associated with the raw materials and the fuel also may be emitted from drying and calcining.

Cyclones, wet scrubbers and fabric filters are the most commonly used devices to control PM emissions from most clay processing operations. Cyclones often are used for product recovery from mechanical processes. In such cases, the cyclones are not considered to be an air pollution control device. Electrostatic precipitators also are used at some facilities to control PM emissions.

Biodegradations

The biological effects of clay minerals are influenced by their mineral composition and particle size. The decreasing rank order of the potencies of quartz, kaolinite, and montmorillonite to produce lung damage is consistent with their known relative active surface areas and surface chemistry. Biodegradations are variable in nature, owing to different types of clay.

Exposure level: Montmorillonite is ubiquitous at low concentrations in soil, in the sediment load of natural waters, and in airborne dust. Biodegradation and bioaccumulation in the food-chain appear minimal, if they occur at all, and abiotic degradation of bentonite into other minerals takes place only on a geological time scale.

There is limited information on occupational exposure to bentonite dust in mines, processing plants, and user industries. The highest reported values for total dust and respirable dust concentrations were, respectively, 1430 and 34.9 mg/m^3, although most values were below 10 mg/m^3 for total dust and below 5 mg/m^3 for respirable dust.

Kaolin is a natural component of the soil and occurs widely in ambient air. Kaolin mining and refining involve considerable exposure, and significant exposure is also expected in paper, rubber and plastic production. Quantitative information on occupational exposure is available for a few countries and industries only. Respirable dust concentrations in kaolin mining and processing are usually below 5 mg/m^3.

Toxicity: An important determinant of the toxicity of clays is the content of quartz. The presence of quartz in the clays studied hampers reliable independent estimation of the fibrogenicity of other components of clays.

General population exposure to low concentrations of montmorillonite and kaolinite, the main components of bentonite and kaolin, respectively, and other clay minerals is ubiquitous. There is no information on the possible effects of such low-level exposure. Long-term occupational exposures to bentonite dust may cause structural and functional damage to the lungs. However, dose–response relationship or even a cause-and-effect relationship cannot be confirmed due to limited information on period and intensity of exposure. From the limited data available from studies on bentonite-exposed persons, retained montmorillonite appears to affect only mild nonspecific tissue changes, which are similar to those that have been described in the spectrum of changes of the "small airways mineral dust disease" (nodular peribronchiolar dust accumulations containing refractile material [montmorillonite] in association with limited interstitial fibrosis). In some of the studies, radiological abnormalities have also been reported.

Long-term exposure to kaolin causes the development of radiologically diagnosed pneumoconiosis, known as kaolinosis. Distinct deterioration of respiratory function and related symptoms has been reported only in cases with prominent radiological findings. Based on data from china clay workers in the United Kingdom, it can be very roughly estimated that kaolin is at least an order of magnitude less potent than quartz. The composition of the clay – i.e., quantity and quality of minerals other than kaolinite – is an important determinant of the effects. Bentonite, kaolin and other clays often contain quartz, and exposure to quartz is causally related to silicosis and lung cancer. Crystalline silica is one of the important components of all clays. The content of crystalline silica will often be the decisive factor in clay-induced adverse health effects. For quartz-induced lung cancer, no reliable quantitative risk estimates can be made.

Statistically significant increases in the incidence of or mortality from chronic bronchitis and pulmonary emphysema have been reported after exposure to quartz.

Bentonite and kaolin have low toxicity to aquatic species, a large number of which have been tested. There is no reason to believe that the mining or processing of bentonite, kaolin and other clays poses significant toxicological dangers to the environment. However, physical disturbance to the land, excessive stream sedimentation, and similar destructive processes resulting from the large-scale mining and processing of clays, like any large-scale mining operation, have a potential for significant environmental damage.

18.4 ENVIRONMENTAL AND HUMAN EXPOSURE DURING CLAY MINING

The information on occupational exposure to bentonite dust in mines reveals a wide range of values for both total and respirable bentonite dust and indicates that very high total dust concentrations can be present in the production of bentonite. The highest values for total dust concentrations were reported by Melkonjan et al. (1981) in their study of bentonite mining and processing in Bulgaria. Only one of the eight types of locations they sampled, inside dump truck cabs during loading, had values consistently below 10 mg/m^3. Their highest reported values, 1150 and 1430 mg/m^3, and highest averages, 504 and 749 mg/m^3, obtained in the vicinity of packing and loading operations, reveal an extraordinary level of dustiness. Values for respirable bentonite dust are generally far below those for total bentonite dust. Silica, which is widely viewed as the major hazard in many industrial dusts (Phibbs et al., 1971; Oudiz et al., 1983; Oxman et al., 1993), was a significant component of bentonite dust, especially in foundries.

Stobbe et al. (1986) analysed mine dusts of West Virginia, USA. Respirable dust samples collected in three locations in the mines contained 64% illite, 21% calcite, 8.5% kaolinite, and 6.7% quartz on average. Processing of china clay involves considerable exposure. Exposure was especially significant before the 1960s (Sheers, 1964). Following drying, nearly all work stages were carried out in high dust concentrations (conveyor belts, bagging and storage in bulk). At present, ventilation is much more effective, and closed technologies are also widely used. Lesser et al. (1978) analysed the free silica content of the airborne dust from a kaolin mill in Georgia and another from South Carolina and noted that while in most of the (total dust) samples free silica was not detectable, in some specimens (three baggers and a bulk loader) quartz was present at approximately 1%. They also said that in all but one of the plants, some baggers and loaders were exposed to about 1% free silica.

There is some relevant information on exposure to illite dust in coal mining and in the manufacture of bricks, but none concerning the mining and processing of relatively pure deposits of illite.

18.5 ENVIRONMENTAL MANAGEMENT IN MINES

This Environmental Health Criteria (EHC) monograph deals with the health hazards associated with bentonite, kaolin and common clay, which are commercially important clay products, as well as the related phyllosilicate minerals like montmorillonite, kaolinite, and illite. Irrespective of mineral mined and the size, most of the mines have adopted environment management system. There is awareness amongst both workers and management. As a result the mines are meeting the consent conditions. Many mines, mostly large scale mechanized and medium scale semi-mechanized mines have gone for ISO 14000 certification of EMS and trying to improve their performance. IBM is organizing Environment Awareness Programme every year and holds regional competition amongst mines where the best performing units are rewarded. In the process and with the influence of NGOs, environment awareness is also growing within the community around the mines. All the mines in organized sector are conscious that their survival depends on sound environmental management and community development programmes. New mines coming up would have to take adequate measures and develop EMS to meet the stringent stipulations of statutes. At the same time statutory authorities have to help in promotion of mining activities for achieving sustainable development. This would also help in developing understanding between the mines and communities.

Overburden is moved, and clays are removed, leaving a depression or pit. State laws usually require levelling or contouring of the disturbed area and planting trees or grasses to prevent or minimize erosion. Ponds for recreational purposes often are created when groundwater levels permit. For processing, the impoundment of slimes and dust control is required. The rules for disposal of coarse tailings are similar to or included within those laws governing reclamation of the mined area.

In order to decrease adverse health effects from occupational exposure to clays, the Task Group recommends that the responsible risk managers:

- set limits for occupational exposure to clay materials, taking into consideration the quartz content;
- enforce and ascertain compliance with the limits by regular exposure monitoring;
- prepare guidelines to ensure good workplace practice;
- disseminate information on the hazards to exposed workers in an appropriate form;
- institute appropriate medical monitoring programmes to protect populations at risk (including pre-employment and periodical medical examinations, including, where appropriate, chest X-ray); and
- oblige clay producers to declare the content of hazardous components, such as quartz, of the saleable products.

18.6 CASE STUDIES

Case study I (Moreno et al., 2008): The Upper Tagus Natural Park is one of the largest and most valuable protected areas in Spain (Guadalajara Province). In this area, a spatial coincidence of extraordinary natural resources takes place. On the one hand, exceptional kaolin deposits occur within sediments of the Upper Cretaceous strata (Utrillas Formation). 30% of the kaolin production of Spain comes from this area, mining being the second economic activity here (13.5% of the local employment). On the other hand, this portion of land supports unique bio and geodiversity in Spain, with distinctive aquatic ecosystems (a Natural Park and two protected habitats of the Natura 2000 network). The most significant environmental problem arises because the kaolin extractive operations create surfaces with high susceptibility to runoff and water erosion, with high potential of on- and off-site ecological effects. The increase of sediments (siltation) of the nearby fluvial network of the Natural Park causes physical pollution of the water, affecting the aquatic wildlife of the protected area.

Geomorphic criteria for the eco-hydrological reclamation of both abandoned and active kaolin mines are taken into account to solve this problem. The proposed landform designs point out that runoff and soil erosion can be reduced to the minimum by building composed concave slopes, whereas the highwalls' geomorphic activity is allowed to be active, although being controlled with drainage systems and retention trenches. It is also recommended that the layout of the reconstructed terrain resembles the local original surficial geomorphology. Finally, the construction of systems of flow control and sediment storage is proposed at the basis of the concave slopes (decanting pools, as small ecologically functional wetlands). For their gauging, the methodology of the International Erosion Control Association (IECA) will be developed.

The kaolin mining activities of the Upper Tagus Natural Park surroundings expose silica sand and kaolin materials, which are easily eroded by splash erosion and running water. This prevents the establishment of soils and vegetation, and has the potential of yielding sediments to the fluvial network. This siltation of the Tagus fluvial network, partially 'natural', but accelerated by kaolin mining activities, is the main management problem of this potected area. Therefore, a geomorphic and hydrologic approach is considered to be essential for the reclamation of the kaolin mines of the Upper Tagus Natural Park. The restoration guidelines of this approach are:

- With the aim of reducing runoff and soil erosion, the building of composed concave slopes is proposed, whereas the highwalls' geomorphic activity has to be controlled with drainage systems and retention trenches.
- A new architecture of surficial deposits and topsoil is recommended, based on the layout of the original structure of the surficial geology of the slopes in which the mine is located.
- The construction of systems of flow control and sediment storage (decanting pools, as small ecologically functional wetlands) are proposed at the basis of the concave slopes, gauged by the methodology of the IECA (Fifield, 2004).

Case study II: When considering the environmental impact of mining on the Fal Estuary, the most important quarrying activity was the production of china clay (kaolinite), principally from the St. Austell area. Historically, china clay mining resulted in the release of both coarse sand as bedload sediment within rivers and also some fine china clay being released in suspension. The early working of china clay was by hand, the river sediment was removed, and then diverted river water was used to separate the coarse sand from the clay, fine sand and mica; a process referred to as 'breaking in the stream'.

The coarse sand settled and was subsequently removed and dumped elsewhere, whilst the remaining clay, fine sand and mica was allowed to settle. The waste sand and mica, along with unrecovered clay was then discharged into the adjacent river catchment. The early study by Everard (1962) on St. Austell Bay clearly demonstrated the impact of the release of china clay into fluvial systems and then out to sea. Indeed the Kernick River was usually referred to as the White River due to its load of china clay. The problem of the release of china clay waste was recognised as early as 1910 when the River Fal became highly polluted and a tax was suggested (Barton, 1966). The discharge of this mine waste into local watercourses continued until 1968 when new legislation caused the practice to stop. Although the discharge of china clay waste no longer occurs, some of the intertidal areas of the estuary are composed of this china clay waste. The release of particulate waste from this mining activity would not cause a significant increase in the amount of heavy metals in the environment. However, this sediment may contain so called 'heavy minerals' which are present within the granite, but subsequently concentrated during the mining activity and the release of this waste material into the rivers. Minerals which may be concentrated in this way would include zircon, monazite and xenotime which geochemically would give an increase in the abundance of Zr, Ce and La and Y respectively. Typically the release of waste from the quarrying of china clay can best be recognised by identifying the minerals present in the clay grain size fraction in the sediment in the estuaries.

Concluding Remarks

This chapter thus highlights all the possible ways by which clay mining can degrade environment; henceforth the chapter also suggests suitable ways to deal with these degradations.

QUESTIONS

1. Explain briefly citing examples how does clay mining cause pollution and state the types of pollutants it gives rise to.
2. Give a schematic sketch showing how different types of pollutants are produced at various stages of clay mining.
3. How does the nature of pollutants vary with mining of different types of clays? Give examples.

4. Kaolin is mined by both dry and wet processes. Which of the two is more beneficial in terms of environmental safety? Illustrate with reasons.
5. Why particulate matters are considered as primary pollutants of concern in clay processing operations? Give a brief note on various types of particulate matters produced during clay mining.
6. State the effects of pollutants on organic world citing examples.
7. How does the exposure level of different types of clays affect the human life?
8. Give a note on various steps taken in environment management in mines.
9. What are the steps needed to be approached in future in enhancing environmental safety in clay mines?

FURTHER READING

Edenfield, R.W. (1960). A clinical and roentgenological study of kaolin workers. *Arch Environ Health*, **1:** 392–403.

Fan, C.M. and Aw, P.C. (1989). Processing of illite powder in Bidor, Perak: a study of the process and the potential uses of illite clay. *Bull Geol Soc Malaysia*, **24:** 67–77.

Fifield, J. (2004). Designing for Effective Sediment and Erosion Control on Construction Sites. International Erosion Control Association. U.S.A.

Grim, R.E. (1968). Clay mineralogy, 2nd ed. New York, McGraw-Hill.

Hosterman, J.W. and Patterson, S.H. (1992). Bentonite and Fuller's earth resources of the United States. Washington, DC. US Geological Survey (USGS Professional Paper 1522).

Lesser, M., Zia, M. and Kilburn, K.H. (1978). Silicosis in kaolin workers and firebrick makers. *South Med J*, **71:** 1242–1246.

Lines, M. (2003). Asian ceramic clays. *Ind Miner*, **427:** 50–55.

Ma, L. and Tang, J. (2002). Refined kaolin in China. Quality improvements needed to meet future paper demand. *Ind Miner*, **415:** 66–71.

Martin Moreno, C., Martin Duque, J.F., Nicolau, J.M., Sanchez, L., Ruiz. R., Sanz, M.A., Lucia, A. and Zapico, I. (2008). A geomorphic approach for the ecological restoration of Kaolin mines at the Upper Tagus Natural Park (Spain). 6th European Conference on Ecological Restoration, Ghent, Belgium.

Melkonjan, A.M., Agekjan F.G. and Muradjan, S.P. (1981). Problems of occupational hygiene in bentonite powder production. *Gig Tr Prof Zabol*, **3:** 19–21 (in Russian).

Moore, P. (2003). Kaolin – White gold or white dirt? *Ind Miner*, **430:** 14–35.

Murray, H.H. (1994). Common clay. *In:* Carr, D.D. (ed.) Industrial minerals and rocks. Society for Mining, Metallurgy, and Exploration, Littleton, Colorado.

Oxman, A.D., Muir, D.C., Shannon, H.S., Stock, S.R., Hnizdo, E. and Lange, H.J. (1993). Occupational dust exposure and chronic obstructive pulmonary disease. *Am Rev Respir Dis*, **148:** 38–48.

Oudiz, J., Brown, J.W., Ayer, H. and Samuels, S. (1983). A report on silica exposure levels in United States foundries. *Am Ind Hyg Assoc J*, **44:** 374–376.

Patterson, S.H. and Murray, H.H. (1983). Clays. *In:* Lefond, S.I. (ed.) Industrial minerals and rocks, 5th ed. American Institute of Mining, Metallurgical, and Petroleum Engineers, New York.

Phibbs, B.P., Sundin, R.E. and Mitchell, R.S. (1971). Silicosis in Wyoming bentonite workers. *Am Rev Respir Dis*, **103:** 1–17.

Sheers, G. (1964). Prevalence of pneumoconiosis in Cornish kaolin workers. *Br J Ind Med*, **21:** 218–225.

Stobbe, T.J., Plummer, R.W., Kim, H. and Dower, J.M. (1986). Characterisation of coal mine dust. *Ann Am Conf Gov Ind Hyg*, **14:** 689–696.

Virta, R.L. (2002). US Geological Survey mineral industry surveys. Clay and shale – 2002. Available at: http://minerals.usgs.gov/minerals/pubs/commodity/clays/claysmyb02.pdf.

CHAPTER

19

ENVIRONMENTAL IMPACTS OF CLAY-RELATED INDUSTRIES

The main aim of this chapter is to highlight the process of various clay-related industries i.e. Fired clay building products industry, Clay brick industry, Vermiculite-related industries etc. and consequently their impact on environmental degradation. Simultaneously the mitigation process also is discussed here. Now-a-days the increasing rate of environmental pollution has become a matter of serious concern. So various methods and technologies have been enunciated to combat the pollution. Derivatives of clays are also used in a number of ways to handle these problems. A glimpse of such applications has been highlighted in this chapter.

19.1 INTRODUCTION

Clays, which are often associated with mineral deposits, can be the source of significant problems in mineral processing operations. Their presence as impurities in low grade ores can lead to issues such as high pumping energy, high water consumption and large volume of tailings. Current strategies for dealing with clay-related issues in mineral processing are all end-of-pipe in nature, in the sense that they all attempt to solve the problems well after they have been created through clay dispersion. However, the effectiveness of such strategies will always be limited due to the physical and chemical nature of clays. Various studies have been taken up to open new paradigm to control clay behaviour in suspensions using a start-of-pipe, or up-front strategy that reduces the level of dispersion and break-up of the clays throughout the process.

Suspended inorganic clays and periphyton are common to aquatic environments, and both can strongly influence physical and chemical water conditions. The uptake rate of soluble reactive phosphorus (from periphytons) by suspended clays in water is tested through artificial stream channels.

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Commercially available kaolinite and bentonite clays were characterized for their aqueous suspension behaviour and affinities for SRP. Periphyton was grown in a recirculating stream system and subjected to simultaneous suspended clay and SRP additions. SRP removal from solution, both in the presence and absence of suspended clays, was used to quantify SRP uptake parameters by periphyton. Clay type and concentrations of 20, 80, and 200 mg l^{-1} had no significant effect upon SRP uptake rate exhibited by periphyton during three 90-min experiments. Less than 1% of SRP removal was attributable to the suspended clay load or artificial stream construction materials, based on clay isotherm data and material sorption studies, indicating that 99% of SRP removal was attributable to biotic uptake. Removal of SRP (as KH_2PO_4) was described by a first-order equation with rate constants ranging between 0.02 and 0.14 min^{-1} (Wolfe and Lind, 2008). Suspended clay was found to reduce Daphnia feeding rates (Kirk, 1991; McCabe and O'Brien, 1983). Under highly turbid conditions, mussels and clams usually close their shells. Turbidity from suspended clay particles significantly reduced the feeding rate of bluegills on Daphnia (Gardner, 1981). In rivers with suspended solid concentrations of 1000-6000 ppm china-clay wastes, brown trout densities were approximately 1/7 of populations in clean (60 ppm) streams (Herbert et al., 1961). These researches also met with some impacts of clay-related industries on environment, which have been attempted to be discussed in this chapter.

19.2 BACKGROUND OF PROBLEMS

The study of clay behaviour in suspensions is important for the optimisation of the mineral processing operations in the industry. Clays, which are part of phyllosilicates family, can be broadly classified into 1:1 and 2:1 phyllosilicates groups according to their structural type. They are often found in mineral deposits, with kaolinite (non-swelling, 1:1 clay mineral subgroup) and montmorillonite (swelling, 2:1 clay mineral subgroup) as the commonly associated clay mineral subgroups in mineral ore bodies. Generally, their presence as impurities in low grade ores is removed through mineral separation processes such as flotation, which rejects these minerals to tailings. These processes utilize a large amount of water as the separating agent. The waste stream, which contains clays and other impurities, is then collected in tailing ponds in order to reduce environmental issues associated with direct disposal to the environment. A wide range of approaches are traditionally adopted to resolve these problems. For example, the use of dispersants to reduce the viscosity of the clay suspension, the addition of polymers or coagulants into the tailings to improve dewaterability, or the use of high pressure dewatering devices to improve the extent and rate of tailings dewatering. A common theme of these approaches is that they are all end-of-pipe in their nature, only tackling the problematic nature of the clay after it has been broken up into individual platelets.

The traditional end-of-pipe approaches to clay-related processing issues generally attempt to address either or both the dispersed and disordered nature of the clay platelets and to promote more efficient packing. However, as has been demonstrated through work in soil science, spontaneous rearrangement of disordered clays into the efficient face-face oriented state cannot occur without the application of significant external pressure (Pashley and Quirk, 1984). Therefore, the benefits of end-of-pipe strategies for the dewaterability of clay suspensions will only ever be moderate (de Kretser et al., 1997). Thus, the single-most effective way to improve clay suspension behaviour is to adopt a start-of-pipe strategy whereby the aim is to minimise the disruption (on wetting) of the face-face oriented packing that is present in the mined clay, as opposed to promoting it from an already disordered state.

The implementation of such a start-of-pipe strategy has been previously investigated to control the dispersion of swelling clays in suspensions. The concept, called ‘controlled dispersion’, was first introduced by Tanihara and Nakagawa (1973) and Deason and Onoda (1984), in which montmorillonite clay swelling behaviour was regulated at the time of initial clay hydration and dispersion, through the suppression of double layer repulsion forces and the substitution of interlayer cations with higher charged cations. By controlling the particle dispersion using coagulant, as opposed to coagulating after the clays had been fully dispersed, significant improvements in dewaterability were observed. The limitation of this early work was the use of commercial clays which would have already undergone an aqueous dispersion process during purification, destroying much of the naturally aligned clay structure.

The work was then continued by de Kretser et al. (1997), in which the dispersion of mined montmorillonitic clays was controlled using $CaCl_2$. Through such control, a clear link between the method of dispersion and the particle size distribution of the resultant suspension was demonstrated, showing that controlled dispersion generates significantly larger particles and fewer fines under identical shear conditions.

However, all of the work on controlled dispersion completed to date has focused on systems where a single component electrolyte is used to regulate clay dispersion. This approach, whilst useful from a proof of concept perspective, is somewhat idealized since all mineral processing streams contain a mixture of different ionic species and the total ionic strength of the process water can vary from low to hyper-saline. Therefore, one of the aims in this study is to gauge the feasibility of implementing controlled dispersion as a practical strategy, via investigation of the effects of overall ionic strength and ion-ion competition on controlled dispersion of run-of-mine swelling clays.

In addition to the work on swelling clays, a method to control the dispersion of non-swelling clays such as kaolin needs to be developed. In terms of mineral processing, non-swelling clays are far more commonly encountered. Thus, if methods were developed for their dispersion control, the potential benefits to industry may be more significant. In general, non-swelling clays such as kaolin possess lower surface charge and correspondingly lower cation exchange capacity than swelling clays (Grim, 1968), making the electrostatically-based methods ineffective. Therefore, a physical cementation via the precipitation of metal hydroxide on the surface of non-swelling clay particles is considered as an alternative approach. Through such process, the mechanical strength of clay aggregates can be increased and the disruption of the close packed structure can be minimised.

Another issue that needs to be considered is that even with an established knowledge on controlled dispersion strategy, the management of such strategy is difficult due to the often sporadic occurrence of clay minerals at the excavation site. The unequal distribution of clays across a mining site means that the severity of clay-related problems – hence the necessity of implementing dispersion control method to mitigate the problems – may vary. From a process risk point of view, the implementation of controlled dispersion strategy may be based on the worst case scenario. However, such operation will result in inefficiencies in terms of water, energy and chemicals consumptions, since routine implementation of the controlled dispersion strategies may not be required. To increase the efficiency of the operation, routine measurements to obtain the mineral profiles of processed ore bodies are required.

Such measurements could indicate the presence of significant levels of clay bearing minerals in the processed ores at any time; hence the occurrence of the clay-related problems can be mitigated through the implementation of controlled dispersion strategies only when necessary.

A wide range of techniques that use optical, infra-red, X-ray, laser, electron or proton beams are available to acquire the mineralogical data of ore bodies. Among all these techniques, X-ray Diffraction (XRD) is the mostly developed and commonly used for clay characterization (Moore and Reynolds, 1997). The benefit of XRD is the identification of different mineral phases from their crystal structures, which allows for classification and quantification of different clay minerals (Moore and Reynolds, 1997). However, the accuracy of this type of measurement can be relatively low for run-of-mine ores. This is due to the significant presence of non-crystalline (amorphous) phase, which cannot be classified into any mineral phase using the XRD technique. Generally, the results from the XRD measurements are normalised by excluding the presence of the amorphous phase; hence the mineralogical data are less reliable for minerals with high amorphous fraction. Therefore, the application of Quantitative Scanning Electron Microscope system (QEMSCAN) as a potential clay mineral characterisation tool is often considered nowadays. This automated technology is capable of providing a routine measurement of the mineralogical data of mineral ore bodies and classification of the amorphous phase that is present in the mineral ores. However, to date its development has been restricted to the evaluation of mineral-of-interest such as base metal sulphide, precious metals, coal, fly ash, mineral sands, oxides and silicates (Sutherland and Gottlieb, 1991; Butcher et al., 2000; Sutherland et al., 2000). Thus, its application to identify the presence and composition of clays has not been fully established.

19.3 ENVIRONMENTAL IMPACT OF DIFFERENT CLAY-RELATED INDUSTRIES

Fired Clay Building Products Industry

Environmental elements relating to the industry are described in the following sections.

Historically the principal elements have been those affecting air quality and to a lesser extent water quality. These and other important issues such as site selection are addressed in the following sub-sections.

The major area of potential environmental impact in this industry is emissions to air. Fugitive emissions from the dryer and kiln processes can, under normal conditions, be considered minimal. Kilns operate under slight negative pressure, using induced draught fans.

Air-borne particulate matter resulting from vehicular traffic, clay extraction, transport and grinding represent the major sources of fugitive dust emission. Best practice fugitive dust emission control procedures are described in the following sections. If clay is transported off-site, or is transferred from another site to the manufacturing facility, the truck should be covered. Truck tailgates should be securely fastened. Vehicular traffic should be restricted to designated internal roadways. Road surfaces should be bitumen sealed, where possible, to prevent fugitive dust generation. Sealed roads should be mechanically swept on a regular basis to minimise dust deposits. Dust generated from unsealed road surfaces within the manufacturing facility should be controlled by the application of water from a mobile tanker. The tanker should also be equipped to handle measured quantities of a suitable wetting or binding agent. Any spillage on road surfaces should be relocated by grading.

Clay quarries are principally worked during the summer months, during the period of maximum fugitive dust generation potential. The area requiring clearing and stripping of top soil should be minimized.

Clay extraction, stockpile formation, and transfers from stockpiles should occur under calm wind conditions, to reduce wind-borne dust. When a clay stockpile is formed, it should be sealed with the application of water. Further wetting is unnecessary unless the surface crust is broken. The stockpile should not be broken up until immediately prior to clay transfer.

Stockpiles are typically formed using scrapers and trucks. Where clay is transferred using a conveyor, the height through which the material falls should be kept to a practical minimum, preferably less than or equal to one metre. Belt scrapers should be fitted to the underside of the belt to remove any clay deposits.

Bays for the storage of clay, and other clay mix additives, should be of three sided construction to act as windshields. Bays should not be filled above these windshields. Transfer of clay or other clay mix additives by conveyor should preferably be conducted on enclosed belts equipped with belt scrapers.

Fugitive dust generated by the grinding process should be controlled by operating at high moisture content, and installing exhaust ventilation system and fabric filtration equipment. Fines collected in the grinding area should preferably be incorporated in the clay mix of an appropriate product or, where this is not possible, returned to the quarry pit and immediately covered with overburden. The transfer of fines to the quarry should only occur under calm wind conditions.

Wastewater is generated by a number of processes at fired clay building product industry sites:

- Stormwater contaminated with suspended solids is generated by runoff from area as such as roadways, plant and equipment, material stockpiles and stripped areas in quarry pits.
- Groundwater infiltration and contaminated runoff from surrounding areas may enter quarry pits.
- Spills of fuels and lubricants can enter surface and groundwater.
- Process wastewater is usually minimal, but the application of metal oxide pigments to roof tiles can generate highly coloured discharges.

Storm-water from surrounding areas should be directed away from fired clay building product industry sites by diversion banks or cutoff drains. Within the site, the potential for stormwater to pick up suspended solids should be minimized. This can be done by sealing roads; minimising the number of stockpiles and locating them away from drainage lines; reducing water velocities; minimising cleared areas; and re-vegetating cleared areas as quickly as possible. Separate dedicated systems should be provided for clean stormwater and contaminated stormwater. Clean stormwater should be discharged to the local drainage system. Fuels, lubricants and other potential contaminants should be stored in hard surfaced, bound areas and facilities to clean up spills should be provided.

Treatment to remove suspended solids will usually be effected by sedimentation ponds. These should be sized to provide effective treatment during high flow episodes. This is crucial; otherwise accumulated sediment may be washed out at times of high flows. Treatment ponds will eventually require desilting and the system should be designed to provide effective treatment while desilting is carried out. This can be achieved by providing bypasses for individual ponds. All discharges of wastes to water from scheduled premises are controlled by EPA works approvals and licences and must comply with them.

The fired clay building products industry generally does not generate wastewater contaminated with industrial wastes. However, the application of metal oxide pigments to roof tiles can produce highly coloured wastewater. Any proposal to discharge wastes to sewer should be referred to the relevant sewerage authority for consideration.

Clay Brick Industry

Energy sources used in the clay brick making process worldwide are dominantly derived from fossil fuels. However, through innovative development it has been shown possible for these traditional sources to be successfully replaced by renewable alternatives reducing greenhouse gas emissions to almost zero. In a further innovative step, it has been possible to introduce a selective blend of solid by-products wastes into the manufactured bricks to partially replace normally quarried clay.

Sustainability stands for the ability to maintain into perpetuity our habitat and lifestyle without exhausting any natural resources. However, the degree of sustainability of a production process can be measured by these criteria:

- Total energy content i.e. the energy that is required to produce, package, distribute, use and dispose of a specific product;
- Consumption of the environment – land for building or mining, forest depilation;
- Emissions – greenhouse gases, dust, other chemical and natural substances;
- Raw materials – non-renewable resources depilation;
- Waste generation – packing, production, use;
- Recyclability – generation of secondary waste cycles;
- Capital – least cost; and
- Durability – longer periods of usage mean lesser consumption of resources.

Energy content: Clay masonry units are usually and generally understood as a sustainable product. The environmental impact of the production process is mostly due to the consumption of energy for the firing of the bricks and quarrying of raw materials. The average direct energy consumption of the production process is to be found ranging between 1.840 and 2.800 kJ/kg of fired brick (of which about 1.50 kJ/kg is electrical). Today bricks are usually fired in a tunnel kiln in which fire remains stationary and bricks are moved on kiln cars through a tunnel divided into preheat, firing and cooling zones. To process energy content of the product, or grey energy, energy contents due to transport and production of raw materials must be added in order to obtain the overall environmental impact. A good assumption is to calculate this additional energy content with about 800 to 1.250 kJ/kg of fired brick. The brick fired with renewable fuels features the least energy content of all building products available in the market today.

Land for mining: Traditional brick production requires extensive mining operations using land. The term "land use" is used to denote those human activities which occupy an area of land. In the field of life cycle assessment, the term “land use” or “land use impacts” is used to denote the environmental impacts related to physical occupation and transformation of land areas. In many areas, mining of raw materials has been greatly reduced by substituting quarried materials with waste materials. Nevertheless quarry operations require great attention in the future in order to further minimize the impact. A measure to reduce the impact of the mining operations is to rebuild mining areas at the end of their useful life.

Emissions of the production process: The emission data for brickyard running on renewable fuels are given in Table 19.1.

Table 19.1: Emission data fossil fuel fired brick/renewable fuels fired brick

Emissions	*Unit*	*Industry*	
		Min	*Max*
Dust		1	30
NO_x as NO_2		10	550
SO_x as SO_2		10	200
Fluoride as HF	mg/m^3	1	120
Chloride as HCl		1	20
Total organic		50	250
Ethanol average	mg/kg brick	3, 1	
Benzol	mg/m^3	1	65
Methanol average	mg/kg brick	5, 7	
Phenol		5	100
Formaldehyde		1	20
Aldehyde (S C1 – C4)	mg/m^3	1	180
Carbon monoxide		< 300	< 1500

Emissions are now being reduced at many brickyards at a considerable rate. It has been possible, as a result of the carbonaceous and fluxing properties of the by-products used in substitution of traditional raw materials and optimization of the feedstock, to reduce the firing temperature of the bricks considerably resulting in a much lower heat requirement than before. The emission of non-fuel related substances such as chlorides and fluorides have been reduced drastically due to optimization of the firing process itself.

Raw materials: The successful introduction of a selective blend of solid by-product wastes into the feedstock replacing quarried raw materials has an immediate effect: The lesser the use of primary raw materials the lesser the environmental footprint of a production process.

Waste generation: During the life cycle of the brick only a very limited amount of waste is generated. Industry studies put the waste generation at around 1.2 g per kg of product. This includes packaging waste at all levels of the production and use phase of the brick itself. At Gasser schemes for recycling any packing material used in shipping the produced clay bricks are in use.

Recyclability: Clay bricks themselves can be recycled without any problems if they have not been contaminated during their use phase with any substances or products that will make it difficult or impossible to recycle them. The substances that might cause problems in recycling bricks are mortars, glues, wire and plumbing, paint and similar substances. It is the obligation of the planner to design for future recyclability by considering how the building can be recycled and possibly disassembled.

Durability: Any construction activity requires resources that are incorporated into the building. These resources are consumed for as long as the building is used. Longer period of usage hence means lesser consumption of resources. A similar concept applies for renovation or modification during the lifecycle of the building itself. The service life of brick buildings is long. The building itself can be adapted to new or changed uses with relatively little effort and expenditure.

Kaolin Wastes

Industrial wastes are responsible for a great part of environment deterioration. The construction industry has the potential to absorb some of these wastes, in the use of mortars and concrete production. Kaolin wastes were used to replace part of or total lime for the manufacture of mortars. These mortars were studied to determine the influence of water/cement ratio on compressive strength. The results were compared with those obtained for cement-lime mortars. Water content was fixed by the flow table standard. The influence of water/cement ratio was more important for the kaolin waste mortars than for cement-lime mortars (Nobrega et al., 2009).

The kaolin industry, in its process of treatment in order to get benefited kaolin, produces a large amount of waste. In this process, two types of kaolin wastes are not properly disposed in the environment. They are placed anywhere in the open air. The irregular disposal of kaolin wastes has turned into a problem for the residents in the surrounding areas of cities. Some studies have shown the potential of these residues in mortars. Both types of kaolin wastes are used. Their mineralogical composition contains kaolinite, mica, quartz and calcite (Nóbrega, 2007). On the whole the fine grains of kaolin wastes caused filler effect in mortars.

Vermiculite-related Industries

Vermiculite, a mineral mined around the world, is used in a variety of commercial and consumer products. After crushing and processing, the raw ore was shipped to many plants in Canada for exfoliation or expanding. At these plants, the ore was heated to about 1000°C causing it to expand like popcorn into a lightweight granular material that is fire-resistant, absorbent, light weight and a good insulator. Vermiculite has been and continues to be used in a variety of building materials. It was made into a variety of insulation products and used as a loose fill insulation inside masonry block walls (the largest volume use), stove pipe and stack insulation, fire separations, cold rooms and in walls and attics of buildings, mostly homes. It is important to understand that not all vermiculites contain asbestos. Some vermiculite mines contain varying amounts of asbestos minerals mixed in the vermiculite deposit. Of particular importance to Canada was the Libby Montana mine owned by W.R. Grace, reported by the U.S Environmental Protection Agency as the source of as much as 70% of the world's consumption until it closed in 1990. The Libby deposit was contaminated with an asbestos mineral usually identified as tremolite. Although W.R. Grace took increasing measures through the history of the operation to reduce the asbestos content in their products, it is likely that most of their production contained at least a trace of free asbestos fibre. Once vermiculite was mixed with a binder (as in concrete and plaster mixes, sprayed, fireproofing, etc.), it is unlikely to ever release significant airborne asbestos. The loose fill products do, however, pose a risk, causing substantial asbestos exposure when disturbed. Exposure to asbestos for prolonged periods or at high concentrations increases the risk of lung cancer and other respiratory diseases. Many of the Libby workers and residents have become sick or died of asbestos disease originating from the mining and milling operations or from the handling and installation of vermiculite insulations. Workers involved in the vermiculite expansion plants have also been afflicted with asbestos disease. In Canada, construction workers are now protected from the hazards of asbestos exposure by detailed health and safety regulations.

Many parties are potentially affected by the asbestos hazard in vermiculite building insulation. The following actions are the minimum necessary to reduce the hazard and liability posed by this material:

- Building occupants or owners with vermiculite insulation need to follow current US EPA recommendations for managing vermiculite in place. In most cases it should be carefully removed prior to renovations or demolition.
- Building/home inspectors should carefully note the type of attic or wall insulation and provide appropriate warning to purchasers.
- Building purchasers should note the presence of vermiculite and include this consideration in buying the property.
- Environmental consultants should incorporate a comment on the presence of apparent vermiculite in all Phase 1 Environmental Property Assessments.
- Laboratories should be very cautious performing vermiculite analysis or certification of "asbestos-free" vermiculite.
- Contractors, construction or demolition workers or persons working in attics or demolishing block walls should note the presence of vermiculite and follow applicable asbestos precautions. In some cases this will require Type 3 precautions.
- Government inspectors, health departments and regulators should note the hazard caused to construction trades and issue appropriate warnings or orders.

Although the percentage of asbestos in the vermiculite may be below the limit normally treated as asbestos, the elevated levels detected upon disturbance indicate that asbestos precautions will be necessary to protect the workers performing removal and to prevent contamination of the rest of the building or home. These precautions include:

- Isolation of the area of removal.
- Use of reduced pressure in the work area to prevent air movement from the site.
- Workers will require protective clothing and asbestos respirators – Powered Air Purifying respirators and a shower for decontamination purposes may be needed.
- Careful cleaning, sealant on all surfaces and clearance air testing will be necessary to document completion.

Attapulgite-related Industries

Attapulgite had been used by industry for more than 40 years before it was recognized as a distinct clay mineral. Chemical composition and some of its properties were sufficiently similar to montmorillonite to cause this confusion. Attapulgite derives its non-swelling needle-like morphology from its three-dimensional crystal structure. The shape and size of the needles result in unique colloidal properties, especially resistance to high concentrations of electrolytes, and give high surface area, high porosity particles when thermally activated. The environmental impacts obtained from attapulgite are as follows:

Oil well drilling fluids: The drilling mud circulated through a well serves the primary function of removing bit cuttings from the hole. In addition, it lubricates the bit, prevents hole sloughing, and forms an impervious filter cake on the walls of the hole, thus preventing loss of the fluid to porous formations. Of utmost importance among the characteristics of a clay for a drilling mud is the ability of the clay to build up a suitable viscosity at a relatively low solids level, and to maintain the desired viscosity throughout the drilling of the well. Bentonite has been widely used for this purpose, but it can be used only with the help of expensive chemical treatments in areas where contaminants such as salt, calcium sulphate, or magnesium sulphate are encountered. Since these contaminants prevent the swelling of bentonite, bentonite is quite ineffective in yielding or maintaining viscosity in their presence. Attapulgite, on the other hand, does not depend on swelling in order to yield viscosity and is quite stable in the presence of these contaminants; it also shows excellent stability under the high temperature conditions encountered in deep drilling in certain areas.

Carrier for agricultural chemicals: The absorbent properties which make attapulgite useful as a floor absorbent also find extensive use in converting pesticides and herbicides to free-flowing granules or dusts. Many of these chemicals are liquids or sticky pastes which would be difficult or impossible to use as produced. Impregnated and absorbed within particles of attapulgite, the chemicals may be readily applied in the field.

19.4 CAUSES FOR ENVIRONMENTAL IMPACT WITH CLAYS

The word "clay" has ambivalent definitions (Bergaya, 2000). On the one hand it is used to define any soil particle smaller than 2 μm, but on the other hand it includes a large group of microcrystalline secondary minerals based on hydrous aluminum or magnesium silicates that have sheet-like structures (Manahan, 2000). There are at least two points that make clay minerals so active in natural processes, and became the key for their wide applications: (a) The very large surface area that arises from the tiny size of the particles (nano-scale), and (b) The fact that those particles are electrically charged, leading to relatively strong electrostatic interactions.

Johnston (1996) developed the concept of "active sites" adopted from biological macromolecules, and defined six different types of sites that may appear in clay minerals, contributing to its interaction with other substances, yielding unique results:

(a) "broken edge" sites and exposed surface aluminol and silanol groups,
(b) isomorphic substitutions,
(c) exchangeable cations,
(d) hydrophobic silanol surfaces,
(e) hydration shell of exchangeable cations, and
(f) hydrophobic sites on adsorbed organic molecules.

The latter active site leads to very interesting interactions between clay minerals and organic chemicals. Changes on the surface of the clay mineral make it specifically optimized for interactions with different types of chemical compounds: Natural clay is negatively charged, and cations can easily bind to their natural surface while negative or non-polar hydrophobic chemicals will be rejected. A hydrophilic behaviour will be observed, based mainly on hygroscopic water bound as hydration shell on the exchangeable cations (Lahav, 1983).

Adsorption of organic cations (e.g., as ammonium based compounds deriving from decaying urine) to the clay-charged sites, exchanging the original-inorganic cations, might exhibit hydrophobic moieties toward the outside surface of the "organoclay" composite.

Such new surface might be optimal to bind non-polar chemicals. In some cases organic cations may be even loaded in excess (charge reversal), leading to interactions with negatively charged chemicals. Morphological properties of the surface also change due to such interactions. Whereas natural smectite shows dense platelets, a sponge-like structure can be obtained by the binding of the natural organic cationic polymer chitosan, to montmorillonite.

19.5 WASTE WATER TREATMENT

Water pollution due to toxic metals and organic compounds remains a serious environmental and public problem. Moreover, faced with more and more stringent regulations, water pollution has also become a major source of concern and a priority for most industrial sectors. Heavy metal ions, aromatic compounds (including phenolic derivatives and polycyclic aromatic compounds) and dyes are often found in the environment as a result of their wide industrial uses. They are common contaminants in waste water and many of them are known to be toxic or carcinogenic.

Strict legislation on the discharge of these toxic products makes it necessary to develop various efficient technologies for the removal of pollutants from waste water. Different technologies and processes are currently used. Biological treatments, membrane processes, advanced oxidation processes, chemical and electrochemical techniques, and adsorption procedures are the most widely used for removing metals and organic compounds from industrial effluents. Amongst all the treatments proposed, adsorption using sorbents is one of the most popular methods since proper design of the adsorption process will produce high quality treated effluents. Adsorption is a well-known equilibrium separation process. It is now recognized as an effective, efficient and economic method for water decontamination applications and for separation and analytical purposes. Various types of clays are significantly used for this purpose.

Clays	
Montmorillonite	Mn^{2+}, Zn^{2+}, Ni^{2+}
Bentonite	Phenol
Organobentonite	Phenol
Sepiolite	Hg^{2+}, Pb^{2+}
Kaolinite	Cu^{2+}, Co^{2+}
Silica Beads	Pb^{2+}, Cd^{2+}
	Dyes

19.6 APPLICATION OF CLAY DERIVATIVES AS POLLUTION-RESISTANTS

- Kaolin clay is used as one of the conventional and frequently used inorganic filler.
- Titanium oxide and calcined clay can be used as filler materials in the preparation of neutral to weakly acidic papers.
- Yan et al. (2005) improved the starch-gel coating method by cooking unmodified starch separately and starch coating was conducted by mixing cooked starch with clay slurry, followed by drying and grinding treatments. The improved method of starch-gel coating does not require any dewatering of the mixture before cooking, and also results in significant increase of strength properties of the filled papers.

- Yoon and Deng (2006) modified clay with starch precipitate using ammonium sulphate as a precipitating agent i.e., the cooked clay mixture is poured into ammonium sulphate solution under stirring to induce the precipitation of starch on the filler surfaces to obtain clay-starch composites. It has been found that clay aggregates with relatively large size can be formed after modification, which may be favourable to the strength development of filled papers.
- Adsorption of toxins from skin or internally by clay organic interaction processes, adsorption of mercury and other heavy metals by ion exchange (Eyton's Earth, 2006), use as an alkalizing agent, supplying alkali exchangeable cations, etc.
- Nowadays procedure for activation of clay honeycomb monoliths has also been introduced. It consists of mixing the clay with coal before extrusion and further burning off the carbon by calcination at the lowest possible temperature that needs to be determined (~440 °C). This treatment improves the textural properties without significantly modifying the structure of the clay minerals. The activation enhances the capacity to remove pollutants (generally methylene blue) from water by adsorption, for a wide range of concentrations. Set of simulated X-ray spectra of minerals used in Rietveld adjustment of clay: (a) anatase, (b) rutile, (c) opal-C, (d) calcite, (e) sepiolite, (f) montmorillonite, (g) kaolinite, (h) illite-muscovite and (i) quartz. Adsorption of methylene blue (MB) is a function of time at room temperature on the clay activated (circles) and clay calcined (squares) monoliths. Initial concentration: 10 mg l^{-1} (white) and 100 mg l^{-1} (black); flow rate: 1200 cm^3 min^{-1}. The proposed method is an easier, more economical and nondestructive way to activate clays if compared with common methods as thermal and acid activation or pillaring. It can be applied using any clay and coal, just properly selecting the mixture composition, minimum temperature to burn-off the carbon, and the additives for extrusion (if needed). In addition, the type and volume of the pores may be adjusted by proper selection of the size of initial carbon particles (Cifredo et al., 2010).

Concluding Remarks

The progressive researches and advanced methodologies pave new dimensions in the domain of impacts of clay-related industries. A glimpse of those practices has been given in this chapter with a view to make it useful to the readers. Researches are still on in an enhanced rate to invent other possible ways of pollution control by the use of clay derivatives. Results with positivity are soon to be expected.

QUESTIONS

1. 'A wide range of approaches are traditionally adopted to resolve these problems.' What are the problems? How the issues are being tackled nowadays?
2. Differentiate between end-of pipe and start-of pipe strategy with respect to their innovation, function and implications.
3. How does the dispersion of non-swelling clays such as kaolin be controlled?
4. On what principles the dispersion strategies for clay minerals are implemented?
5. State the role of analytical techniques in implementing controlled dispersion strategies.
6. Give a chart showing various products manufactured in different clay-related industries.
7. How can the adsorption property of clay minerals be used in waste water treatment?
8. What do you mean by the term clay derivatives? State their applications in pollution reduction.

FURTHER READING

Bergaya, F.A. (2000).. Clay science studies in the world. Proceedings of the 1st Latin American Clay Conference, Funchal, Madeira, **1:** 1-3.

Butcher, A.R., Gravestock, D.I., Gottlieb, P., Cubitt, C. and Edwards, G.V. (2000). A new way to analyse drill cuttings: A case study from Deparanie I, Copper Basin, South Australia. *APPEA Journal*, 774-775.

Cifredo, G., Gatica, L.M., Harti, S. and Vidal, H. (2010). Easy route to activate clay honeycomb monoliths for environmental applications. *Applied Clay Science*. **47:** 392-399.

de Kretser, R.G., Scales, P.J. and Boger, D.V. (1997). Improving clay-based tailings disposal: A case study on coal tailings. *AIChE Journal*, **43(7):** 1894-1903.

Deason, D.M. and Onoda, G.Y. (1984). Controlled dispersion of clays and its effects on phosphate clay dewatering. *Min. Metall. Proc.*, **1(2):** 149-152.

Eytons' Earth (2006). Internal uses of Healing Clays. http://www.eytonsearth.org/general-uses-clay.php

Gardner, M.B. (1981). Effects of turbidity on feeding rates and selectivity of bluegills. *Transactions American Fisheries Society*, **110:** 446-450.

Grim, R.E. (1968). Clay mineralogy. McGraw Hill, N.Y.

Herbert, D.W.M., Alabaster, J.S., Dart, M.D. and Loyd, R.L. (1961). The effect of china clay wastes on trout streams. *International J. Air and Water Pollution*, **5(1):** 56-74.

Johnston, C.T. (1996). Sorption of Organic Compounds on Clay Minerals: A Surface Functional Group Approach. *In:* CMS Workshop Lectures, **8**, Organic Pollutants in the Environment. Sahwney, B. (Ed.). The Clay Mineral Society, Boulder CO, 1-44.

Kirk, K.L. (1991). Suspended clay reduces *Daphnia* feeding rate: Behavioral mechanisms. *J. Freshwater Biology*, **25:** 357-365.

Lahav, N. (1983). Fundamentals of Soil Science (in Hebrew). Academon Press, Rehovot, Israel.

Manahan, S.E. (2000). Environmental Chemistry. 7th Ed. CRC Press, Boca Raton FL.

McCabe, G.D. and O'Brien, W.J. (1983). The effects of suspended silt on feeding and reproduction of *Daphnia* pulex. *American Midland Naturalist*, **110(2):** 324-337.

Moore, D.M. and Reynolds, R.C., Jr. (1997). X-ray diffraction and the identification and analysis of clay minerals. 2nd edition. Oxford University Press, New York.

Pashley, R.M. and Quirk, J.P. (1984). The effect of cation valency on DLVO and hydration forces between macroscopic sheets of muscovite mica in relation to clay swelling. *Colloids Surf.*, **9(1):** 1-17.

Sutherland, D.N. and Gottlieb, P. (1991). Application of automated quantitative mineralogy in mineral processing. *Minerals Engineering*, **4(7-11):** 753-762.

Sutherland, D.N., Gottlieb, P. and Butcher, A. (2000). Mineral characterisation in the 21^{st} century. International Symposium on Minerals and Metals: Challenges Beyond 2000, IIM, Bhilai.

Tanihara, K. and Nakagawa, M. (1973). Flocculation of bentonite suspensions under the supression of swelling with an inorganic electrolyte. *Nip. Kagaku Kaishi*, **5:** 923-930.

Wolfe, J.E. and Lind, O.T. (2008). Influence of suspended clay on phosphorus uptake by periphyton. *Hydrobiologia*, 610:211–222 DOI 10.1007/s10750-008-9436-7.

Yan, Z., Liu, Q. and Deng, Y. (2005). Improvement of paper strength with starch-modified clay. *J. Appl. Polym. Sci.*, **97:** 44-50.

Yoon, S.Y. and Deng, Y. (2006). Clay-starch composites and their application in papermaking. *J. Appl. Polym. Sci.*, **100:** 1032-1038.

CHAPTER

20

RECYCLING OF INDUSTRIAL WASTE PRODUCTS

The use of recycled materials reduces waste shipped to landfills and cuts down on mining of clay and other minerals needed to make conventional tile. Recycling also reduces energy use because making a product from waste material typically requires less energy than fabricating one from raw materials. This, in turn, helps to slash fuel use in manufacturing and helps reduce environmental pollution.

20.1 INTRODUCTION

Environmental pollution is the major problem associated with rapid industrialization, urbanization and rise in living standards of people. For developing countries, industrialization was must and still this activity very much demands to build self reliance and in uplifting nation's economy. However, industrialization on the other hand has also caused serious problems relating to environmental pollution. Therefore, wastes seem to be a by-product of growth. The country like India can ill-afford to lose them as sheer waste. On the other hand, with increasing demand for raw materials for industrial production, the non-renewable resources are dwindling day-by-day. Therefore, efforts are to be made for controlling pollution arising out of the disposal of wastes by conversion of these unwanted wastes into utilizable raw materials for various beneficial uses. The problems relating to disposal of industrial solid waste are associated with lack of infrastructural facilities and negligence of industries to take proper safeguards. The large and medium industries located in identified (conforming) industrial areas still have some arrangements to dispose solid waste. However, the problem persists with small scale industries. In a number of cities and towns, small scale industries find it easy to dispose waste here and there and it makes difficult for local bodies to collect such waste though it is not their responsibility. In some cities, industrial, residential and commercial

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areas are mixed and thus all waste gets intermingled. Therefore, it becomes necessary that the local bodies along with State Pollution Control Board (SPCB) work out requisite strategy for organising proper collection and disposal of industrial solid waste.

Materials like clay, sand, stone, gravels, cement, brick, block, tiles, distemper, paint, timber and steel are being used as major building components in construction sector. All these materials have been produced from the existing natural resources and will have intrinsic distinctiveness for damaging the environment due to their continuous exploitation. Nevertheless, during the process of manufacturing various building materials, especially decomposition of calcium carbonate, lime and cement manufacturing, high concentration of carbon monoxide, oxides of sulphur, oxides of nitrogen and suspended particulate matter are invariably emitted to the atmosphere.

Clays are used to make pottery, which was in turn used to hold food and grains or items for barter and trade. Pottery and similar vessels were reused and repaired until they wore out or were broken. Landfills are now usually built with a flexible liner, made of clay or a synthetic material that is used to cover the bottom and sides of the facility. The liner helps to keep any gases or liquid (known as leachate) from migrating out of the landfill.

Unlike sanitary landfills, whose sides and bottom are lined with clay for another barrier layer to prevent the leaching of toxins into the water table, the Chef Menteur site was unprotected and did not have a leach detection system installed when it opened. Officials for the operator noted that the site was naturally clay lined and had been used successfully for years as a landfill for household waste.

20.2 GENERATION OF WASTE

Growth of population, increasing urbanization, and rising standards of living due to technological innovations have contributed to an increase both in the quantity and variety of solid wastes generated by industrial, mining, domestic and agricultural activities. Globally the estimated quantity of wastes generation was 12 billion tonnes in the year 2002 of which 11 billion tonnes was industrial wastes and 1.6 billion tonnes municipal solid wastes (MSW). About 19 billion tonnes of solid wastes is expected to be generated annually by the year 2025 (Yoshizawa et al., 2004). Annually, Asia alone generates 4.4 billion tonnes of solid wastes and MSW comprises 790 million tonnes (MT) of which about 48 (6%) MT is generated in India (Yoshizawa et al., 2004; CPCB, 2000). By the year 2047, MSW generation in India is expected to reach 300 MT and land requirement for disposal of this waste would be 169.6 km^2 as against which only 20.2 km^2 was occupied in 1997 for management of 48 MT (CPCB, 2000).

The heterogeneous characteristics of the huge quantity of wastes generated lead to complexity in recycling and utilization. The comparative physico-chemical characteristics of solid wastes generated from hazardous and non-hazardous sources over clay and cement are shown in Tables 20.1 and 20.2,

Table 20.1: Comparative physical characteristics of solid wastes generated from hazardous and non-hazardous sources over sand and clay soil

Sl. No.	*Characteristics*	*CCRs*	*Jarosite*	*Copper slag*	*Red mud*	*Marble dust*	*Sand*	*Clay (Kaolinite)*
1	Particle size (µm) (D_{80})	130-260	14-23	<150	<20	43.9–103.1	300-600	<15
1	Bulk density (g/ce)	0.96-1.25	0.97-1.0	1.44-1.62	1.36-1.6	1.87	1.59	1.48
2	Specific gravity	2.08-2.3	2.92-3.0	2.8-3.8	2.6-3.4	2.51-2.76	2.64	2.37-2.56
3	Porosity (%)	37.45-37.5	66.5-67.7	–	49.26-54.66	39.65-49.0	68.41	36.31
4	pH	6.98-7.03	6.7-6.85	<5.70	11-12.5	8.36-9.5	8.18	7.64
5	EC (µmohs/cm)	491.65-504.24	13260-14090	500.56	495-766.48	276.94-500	246.11	6506.67

Table 20.2: Comparative chemical characteristics of solid wastes generated from hazardous and non-hazardous sources over cement and clay soil

Sl. No.	*Constituents in %*	*CCRs*	*Jarosite*	*Red mud*	*Marble waste*	*Copper slag*	*Phospho-gypsum*	*Cement OPC*	*Clay (Kaolinite)*
1.	SiO_2	55.9-57.6	2.91-4.0	5-13.5	1.69-8.5	28.0–32.0	2.41	19.7-22.62	42.09-61.54
2.	Al_2O_3	16.0-24.0	0.70-4.4	10-23	1.3-6.1	2.4-6.8	<0.5	4.93-6.6	28.65-32.9
3.	Fe_2O_3	5.38-6.34	51.28	28-56	0.25-3.66	44-47.70	<0.5	3.19-3.5	11.77-12.88
4.	CaO	0.25-6.5	0.98-12.0	8-17	29.5-55.4	1.65-6.60	32-41	63.0-64.0	0.13-2.22
5.	MgO	1.01-1.34	1.81-1.94	0.35	4.04-20.6	0.75-2.54	0.10	0.7-2.38	2.04-2.63
6.	K_2O	1.62-2.13	0.71-0.75	0.39-0.50	0.01-1.9	0.61	<0.02	0.55-0.6	0.74-3.51
7.	ZnO	1-2.6	13.29	<0.5	NA	0.005-1.30	NA	NA	NA
8.	PbO	<0.1	1.8-2.04	<0.2	NA	0.002-0.28	4-5.11	NA	NA
9.	CuO	<0.1%	0.46-1.65	<0.2	NA	0.46-3.76	3.42-17.6	NA	NA
10.	LOI	1.53-	>12.6	6-14	40.6-43.46	<1	19.20	0.3-1.75	<12.55

NA–not analysed.

respectively (Agarwal et al., 2004; Ashokan, 2004; Bhattacharyya et al., 2004; Garg, 1996; Saxena and Ashokan, 2002; Yalcm and Sevinc, 2000). The physico-chemical properties of solid wastes depend on the properties of feed raw materials, mineralogical origin, operating process and their efficiency. It is evident from the characteristics of these wastes, generated from different processes, that they have good potentials for recycling and utilization in developing various value-added building components. Use of industrial wastes and by-products as an aggregate or raw material is of great practical significance for developing building material components as substitutes for the traditional materials and providing an alternative or supplementary materials to the housing industry in a cost effective manner. In order to effectively utilize all these solid wastes, efforts have been made and mathematical models were also established universally and as a consequence considerable quantity of wastes is now being recycled and used to achieve environmentally sound management (Haque, 2000).

Fired clay bricks are generated as a waste product from construction and demolition activities, and their value is an additive in the manufacture of PC-based construction products. It was established that the aluminosilicate phase in the fired clay bricks promoted the development of the tobermorite, the principal binder in most calcium silicate products under hydrothermal conditions. The use of CB waste as a cement replacement for the manufacture of these products was also demonstrated as a viable option.

20.3 OBJECTIVES

The main objectives regarding any waste recycling process are to obtain ceramic composites from fly-ash and building materials from drilling fluids and slag, and to use them in the impermeable layers of roads. It aims to demonstrate the viability of a novel technology for the recycling of fly ash, drilled solid wastes and steelmaking slag. Specific objectives are to:

- Select and fully characterise the types of wastes (fly ash, drilled solid wastes, metallurgical slag);
- Identify potential secondary raw materials that could replace primary ones;
- Formulate optimal methods and technologies for processing the target wastes;
- Design and build an improved waste processing pilot plant;
- Test at pilot scale the process for manufacturing ceramic composites from secondary materials; and
- Demonstrate that the use of natural resources and energy can be significantly reduced by harnessing the potential of the target waste streams, thereby achieving sustainable waste management.

Steps should be taken to:

- Reduce the amount of waste going to landfill;
- Save natural resources by recycling fly-ash, oil drilled wastes and metallurgical slag instead of using raw minerals;

- Save energy with respect to traditional processes for producing building materials;
- Reduce the carbon footprint associated with the production of building materials, and reduce the energy consumed in conventional raw materials recovery (clay, clay sand, feldspar, etc.);
- Recover and recycle a total of 50% of the target wastes;
- Demonstrate that it is possible to replace with fly ash 30-50% of the natural sand used in manufacturing ceramic products;
- Show that 100,000 tonnes/yr of well-drilled solids (cake) could be used to manufacture bricks in place of clay. Since preliminary milling is not required, this would result in a 24,000 tonne/yr reduction in CO_2 emissions and cost savings at building materials factories; and
- Demonstrate that some 500,000 tonnes/yr of metallurgical slag (with 50% CaO quicklime, content an average) could be used in cement manufacturing, replacing 270,000 tonnes/yr of quicklime extraction and saving 280,000 tonnes/yr in CO_2 emissions.

20.4 RECYCLING

Recycling generally refers to the separation of materials in the waste stream so that some of those materials can be reused. Re-cycling is highly dependent on two factors: the availability of re-cycled goods supplies and the market for those goods. From 1994 to 1997, for instance, the United States experienced a glut of paper that had been collected for recycling; the market for old newspapers dropped off, as did prices, and some communities even had to store paper in warehouses as they waited for the prices to rise again. Recycling is considered one of the best types of waste management because it can stretch the capacity and life of landfills by reducing the volume of materials considered as trash, while reducing the amount of virgin material that is needed for products and packaging. According to the Bureau of International Recycling, without recycling, a substantial number of end-of-life goods would end up in landfills, representing an environmental and economic loss because the materials they contain would be lost to the production cycle forever (Bureau of International Recycling, 2007).

Three types of recycling methods are used.

Source separation: Households and businesses separate their recyclable items from other waste at the source where they are created, placing material into small containers or bins by type (paper, glass, plastic). Processing is usually conducted by scrap dealers or taken to a consolidation site for sale to another processor.

Container separation: Large bins or containers are used to separate waste into three categories: non-recyclable waste, organic waste, and recyclables. Once at the collection facility, the recyclables are separated out by type, sometimes by manual sorting. Some communities rely on a bag system, with all recyclables placed in a visually distinct blue bag for collection (blue bags differentiate recyclables from trash and yard waste, the bags for which are usually black or green).

Commingled collection: All waste is commingled and collected by a single truck. Recyclable materials are sorted and processed by mechanical means including magnets and shredders. This method is sometimes called front-end processing or refuse-derived fuel processing.

Most recycling efforts focus on homeowner or community involvement, such as the provision of bins by the local government to home dwellers so that items can be picked up at the curbside as a regular part of trash collection services. Other areas have experimented with drop-off stations for items such as paint, appliances, consumer electronics, and Christmas trees, which are then recycled and processed depending on the type of material. Another strategy is a buy-back programme, a low-cost, centralized operation whereby items such as aluminum cans or glass bottles can be given to a recycler for a fixed amount of payment, such as by the pound. This method is most successful in states that have bottle deposit laws, which encourage recycling and reduce the amount of waste that must be landfilled or incinerated.

Recycling thus mainly focuses on:

- Installation of closed-loop systems;
- Recycling off site for use; and
- Exchange of wastes.

Waste minimisation at source may be achieved within the industry through application of various approaches described above. The systems for waste minimisation, utilisation and recycling are schematically shown in Fig. 20.1.

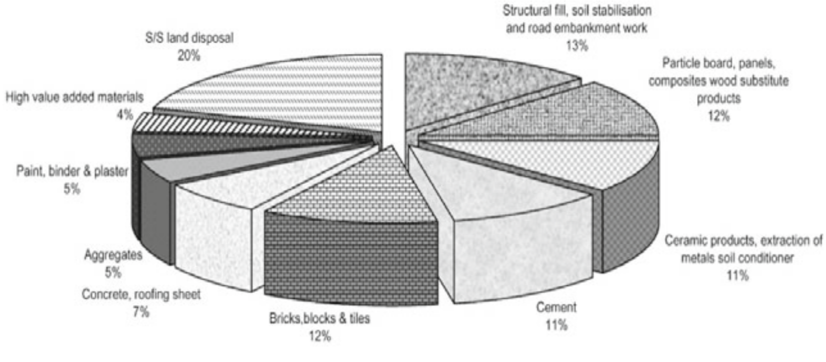

Fig. 20.1. Future potentials for solid waste recycling and utilization.

Importance of Recycling

Waste recycling is the reprocessing of old materials into new products. Basically, it is for the prevention of wastage of potentially useful materials. In present days, importance of waste material recycling and industrial recycling is becoming greater of a concern for the benefit of economy as well as environment. As planet earth has limited resources, waste material recycling becomes extremely important virtually in all industrial applications. The world economy cannot sustain the depletion of natural resources in the same pace. The importance of industrial waste recycling is now held in high regard. Most of the waste materials can be recycled to turn them into usable substance. Today, various legislative regulations are enforced by local and international authorities in regard of waste material recycling. The importance of industrial recycling is also extended to businesses, as they spend less on production costs. This ensures a overall reduced costs that encourage consumption. The detailed benefits of waste material recycling include:

- Reduction of the usage of fresh raw materials
- Preserving natural resources
- Reduction of energy usage
- Less power consumption in recycling
- Reduction of air and water pollution
- Reduction for traditional waste disposal
- Reduction of pollution caused by waste
- Reduction in the release of harmful chemicals and greenhouse gases from rubbish
- Saves space required as Waste Disposal Landfill
- Reduce financial expenditure in the economy
- Preserve natural resources for future generations

20.5 WASTE TREATMENT PROCESSES

Waste management is the collection, transport, processing, recycling or disposal, and monitoring of waste materials. Concern over environment is being seen as a massive increase in recycling globally, which has grown to be an important part of modern civilization. The consumption habits of modern consumerist lifestyles are causing a huge global waste problem. Industrialization and economic growth has produced more amounts of waste, including hazardous and toxic wastes. There is a growing realization of the negative impacts that wastes have had on the local environment (air, water, land, human health etc.).

Waste management is the collection of all thrown away materials in order to recycle them and as a result decrease their effects on our health, our surroundings and the environment and enhance the quality of life. Waste management practices differ for developed and developing nations, for urban and rural areas, and for residential and industrial producers. Waste management flows in a cycle: monitoring, collection, transportation, processing, disposal or recycle. Through these steps a company can effectively and responsibly manage waste output and thus have positive effects on the environment.

Waste generation per capita has increased and is expected to continue to climb with growing population, wealth, and consumerism throughout the world. Approaches to solving this waste problem in a scalable and sustainable manner would lead us to a model that uses waste as an input in the production of commodities and value monetized, making waste management a true profit centre. The conversion of waste as a potential source of energy has a value as a supplemental feedstock for the rapidly developing bio-fuels sector. A variety of new technologies are being used and developed for the production of biofuels which are capable of converting wastes into heat, power, fuels or chemical feedstock.

Thermal technologies like gasification, pyrolysis, thermal depolymerization, plasma arc gasification, and non-thermal technologies like anaerobic digestion, fermentation etc. are a number of new and emerging technologies that are able to produce energy from waste and other fuels without direct combustion. Biodegradable wastes are processed by composting, vermicomposting, anaerobic digestion or any other appropriate biological processing for the stabilization of wastes. Recycling of materials like plastics, paper and metals should be done for future use.

There is a clear need for the current approach of waste disposal in India that is focussed on municipalities and uses high energy/high technology, to move more towards waste processing and waste recycling (that involves public-private partnerships, aiming for eventual waste minimization) driven at the community level, and using low energy/low technology resources.

Some states have adopted a process for selecting which types of techniques, technologies, and management programmes they should use for achieving waste management objectives, including four methods identified by the EPA: source reduction, recycling and composting, combustion, and landfills. Many states and communities then prioritize these options in order of preference because of the environmental impacts of each one. California, for instance, has chosen a hierarchical process that gives preference to source reduction, followed by recycling and composting, waste transformation, and landfilling. Combustion has been replaced by waste transformation as an option in that state, although the process still requires that recycling be considered only after the maximum amount of source reduction has been achieved (Tchobanoglous and Kreith, 2002).

Case study I: RM-10 is a proprietary blend of clay minerals, polymers and pH adjusting agents, which allow one-step entrapment of emulsified oils and dissolved metals from various waste streams. CETCO Oilfield Services has been the industry leader in clay-based flocculants and for over 30 years has provided the trusted line of RM-10 products to remove the following contaminants from waste streams:

- Heavy metals
- Oils and grease
- Suspended solids

How RM-10® treatment works

1. Chemical components adjust the pH of the water which enhances the precipitation of metals and breaks oil emulsions.
2. Bentonite clay particles attract and encapsulate precipitated metallic ions.
3. The polymeric portion of the formulation attracts remaining oils and suspended solids and forms a floc, which settles to the bottom of the treatment vessel.
4. The bentonite clay and polymer work together to create a strong filterable floc, which will encapsulate and contain heavy metals while allowing the floc to readily release water resulting in a drier sludge cake.

The entire process is completed in just a few minutes, resulting in clear water that can be discharged directly to a POTW or recycled. The sludge and its encapsulated contaminants are highly resistant to leaching and can be generally disposed of as a non-hazardous waste.

20.6 USE OF CLAY IN WASTE MANAGEMENT

Clay Liners

Compacted clay liners are fundamental elements in lining systems of industrial and domestic waste disposal sites. In tropical countries, lateritic clays are suitable materials for the construction of clay liners because of their availability and their appropriate geotechnical properties. Furthermore, such soils have been extensively used in recent decades in dam and road construction. However, little is known about the geomechanical and chemical parameters of lateritic soils for the performance-oriented design of lining systems (Manassero et al., 1998). Lateritic clays are basically composed of quartz, kaolinite, aluminium hydroxide (gibbsite) and iron oxide (hematite). The oxides and hydroxides accumulate and adhere to the surface of the clay minerals, acting as natural cements and forming water-stable micro-aggregates. Therefore, expansion and strength loss in presence of water are well beneath expected values, as related to the expressive clay content. The mineralogy signals to a low adsorption capacity; however, significant cation retention has already been observed in these soils (Boscov, 1977). Diffusion may be an important migration mechanism of metal transport in acidic solutions through a compacted lateritic clay. However, some metals are retained in the soil even at pH 1.

At pH 1, some metals were extracted from the soil, whereas others were retained in the specimen upper layer. For some metals, at least 85% of the solute mass applied to the system was retained in the first 1 or 2 centimetres. Metal solutions at low concentrations and very acidic environment may cause desorption of previously adsorbed cations or dissolution of soil minerals. At pH 4, hydrolysis and the high soil adsorption led to very low concentrations in the soil pore water. Less than 1% of the initial concentration of the test solution was detected in the soil pore water for most metals, and less than 15% for all metals, i.e. soil retention was enhanced. Comparison of results at pH 1 and pH 4 testifies the importance of pH correction for contaminated wastes, i.e., a situation of migration by diffusion with low retention can be changed to that of high retention in the upper centimetres of the clay liner (Boscov et al., 1999).

Construction and Demolition (C&D) waste typically consists of concrete, bricks, asphalt, wood, glass, masonry, roofing, siding and plaster, alone or in combinations. Intermediate C&D landfills must have a 3-foot-thick clay liner and a leachate collection system. The diameter of leachate collection pipes must be at least six inches. Engineered landfills for municipal and industrial waste are constructed with a base liner and a leachate collection system. The primary purpose of the liner is to prevent groundwater pollution. The liner may consist of clay only or be a combination of geomembrane and clay (known as a composite liner). The liner is constructed with at least a 2% slope towards perforated leachate collection piping to direct leachate to a collection system.

The minimum thickness of a clay liner is five feet except in intermediate C&D landfills where three feet is allowed. In a composite liner, a 60-mil or thicker geomembrane is placed directly over a 4-foot-thick clay liner. Composite liners are required for all new municipal waste landfills. The maximum allowable slope of inside walls of a landfill is three horizontal to one vertical. In clay-lined landfills, leachate transfer lines may penetrate the liner horizontally at the perimeter berm. An antiseep collar is placed around the transfer line penetrating the liner to minimize the escape of leachate. In composite-lined landfills, on the other hand, leachate is pumped from the landfill's leachate collection system inside a sideslope riser – a large-diameter pipe that extends from a sump at the base of the landfill to the top of the berm.

Fine-grained soil as defined by the Unified Soil Classification System (USCS) is used for clay liner construction. According to USCS a soil is classified as fine grained if a minimum of 50% of a given sample by weight passes through the 200 sieve. In addition, the clay used for liners must have:

- a saturated hydraulic conductivity of 1×10^{-7} cm/sec or less after compaction,
- an average liquid limit of 25 or greater with no values less than 20, and
- an average plasticity index of 12 or greater with no values less than 10.

Because freezing and thawing increase the permeability of clay, newly constructed liners must be protected from freeze-thaw damage using four feet of solid waste or other frost protection material during winter months. Both the base liner and the lower 10 feet of the inside slopes are required to be protected from freeze-thaw damage.

While constructing clay liners, clods larger than four inches should be broken up and the lift heights must not be greater than six inches after compaction. The clay must be compacted to 90% modified or 95% standard Proctor density at or wet of optimum moisture content using a sheep's foot roller with a minimum weight of 30,000 pounds.

State codes require the following tests to demonstrate the constructed quality of landfill clay liners and final cover clay layers: dry density and moisture content, grain size analysis up to 0.002 millimetre particle size, Atterberg limits, and hydraulic conductivity of field samples.

Waste placed in a unit can interact with compacted clay liner materials, thereby influencing soil properties such as hydraulic conductivity and permeability. Two ways that waste materials can influence the hydraulic conductivity of the liner materials are through dissolution of soil minerals and changes in clay structure. Soil minerals can be dissolved, or reduced to liquid form, as a result of interaction with acids and bases. For example, aluminium and iron in the soil can be dissolved by acids, and silica can be dissolved by bases. While some plugging of soil pores by dissolved minerals can lower hydraulic conductivity in the short term, the creation of piping and channels over time can lead to an increased hydraulic conductivity in the long term. The interaction of waste and clay materials can also cause the creation of positive ions, or cations. The presence of cations such as sodium, potassium, calcium and magnesium can change the clay structure, thereby influencing the hydraulic conductivity of the liner. Depending on the cation type and the clay mineral, an increased presence of such cations can cause the clay minerals to form clusters and increase the permeability of the clay. Therefore, before selecting a compacted clay liner material, it is important to develop a good understanding of the composition of the waste that will be placed in the waste management unit. EPA's Method 9100, in publication SW-846, measures the hydraulic conductivity of soil samples before and after exposure to permeants.

If a risk evaluation recommended the use of a single liner, another option to consider is a geosynthetic clay liner (GCL). GCLs are factory-manufactured, hydraulic barriers typically consisting of bentonite clay (or other very low permeability materials), supported by geotextiles or geomembranes held together by needling, stitching, or chemical adhesives. GCLs can be used to augment or replace compacted clay liners or geomembranes, or they can be used in a composite manner to augment the more traditional compacted clay or geomembrane materials. GCLs are typically used in areas where clay is not readily available or where conserving air space is an important factor.

Clay in Ceramics

As solid wastes are becoming a matter of increased world concern due to their amount as well as difficulty and cost of final disposal, ceramic products can well supply as matrices for industrial residues incorporation such as giving an option for the solid waste disposal with a possible increase in the properties of the clay ceramic products. The incorporation of wastes from several industrial activities is a technological alternative to reduce the environmental impact due to their indiscriminate disposal. One such measure is the waste incorporation into intensive-produced clay ceramics like bricks and tiles (Parsons et al., 1997). This incorporation is now a common practice and benefits both, the industry that generates the waste and the ceramic industry that saves on the clay, which is its basic raw material. In some cases the incorporation also improves the properties of the ceramic product (Oliveira and Holanda, 2004). Research works on the structural and physical changes that wastes – mainly industrially produced – cause to the final ceramic product has been rapidly expanding in these last two decades (references in Vieira and Monteiro, 2009). In spite of these examples of a continuous effort to incorporate wastes into clay ceramic motivated by technical and economical advantages, environmental issues are still a matter of concern. The firing stage during the clay ceramic process can promote the elimination of potentially toxic constituents present in the solid residues through their volatilization. However, the gas emission due to the clay firing process and its related atmospheric pollution may be enhanced as a consequence of an incorporated waste (Souza et al., 2008). It is known that the firing of clay ceramics in conventional furnaces using fuels such as wood, charcoal, heavy oil and natural gas generates appreciable amounts of gaseous components, mainly carbon dioxide (CO_2), carbon monoxide (CO) and methane (CH_4). In addition to the atmospheric pollution, these gas sets could be harmful to the human health and can corrode equipments (Morgan, 1993). Works on the effect of gas emission caused by the firing of clay ceramics incorporated with industrial wastes are practically inexistent.

Concluding Remarks

Recycling thus paves the way for new methodologies in combating environmental pollution and introducing variability in potential uses of different industrial products.

QUESTIONS

1. State with respect to nationalized domain the need for requirement of nationalized wastes.
2. How the industrial waste recycling can be related to clay-related industries?
3. Is always the rate of waste generation at par with the rate of waste recycling? Illustrate.
4. Cite examples with respect to different types of clay related industries, how the gernerated wastes can be recycled?
5. Comment on the objectives proposed for recycling of clay wastes.
6. How the steps followed in clay waste recycling can be extrapolated in terms of other similar category of industries?
7. Illustrate the relation between waste recycling and waste treatment stating their individual environmental implication.
8. State the properties of clays on the basis of which their potential for being used as liners or ceramics can be assigned?

FURTHER READING

Agrawal, A., Sahu, K.K. and Pandey, B.D. (2004). Solid waste management in non-ferrous industries in India. *Conservation and Recycling*, **42:** 99-120.

Bhattacharyya, J.K., Shekdar, A.V. and Gaikwad, S.A. (2004). Recyclability of some major industrial solid wastes. *Journal of Indian Association for Environmental Mangement*, **31:** 71-75.

Boscov, M.E.G. (1977). Contribution to the design of mineral barriers for hazardous waste disposal sites using lateritic soils. Doctorate thesis. Universidade de São Paulo, São Paulo, Brazil. (in Portugese)

Boscov, M.E.G., Oliveira, E., Ghilardi, M.P. and Silva, M.M. (1999). Metal diffusion through a lateritic compacted clay. Proceedings 4th Brazilian Conference on Geo-Environmental Engineering (REGEO99). São José dos Campos, Brazil. (in Portugese)

Central Pollution Control Board (CPCB) (2000). Report on management of municipal solid wastes, Delhi, India.

Garg, M., Singh, M. and Kumar, R. (1996). Some aspects of durability of a phosphogypsum-lime-fly ash binder. *Construction and Building Materials*, **101(4):** 173-279.

Haque, A., Mujtaba, I.M. and Bell, J.N.B. (2000). A simple model for complex waste recycling scenarios in developing economics. *Waste Management*, **20:** 625-631.

Manassero, M., Parker, R., Pasqualini, E., Szabo, I., Almeida, M., Bouazza, A., Daniels, D. and Rowe, R.K. (1998). *In:* Controlled landfill design – Geotechnical aspects. TC5 Report, Proceedings 3rd ICEG, Vol. 3, Lisbon, Portugal.

Morgan, D.J. (1993). Thermal analysis including evolved gas analysis of clay raw materials. *Applied Clay Science*, **8:** 81.

Oliveira, G.E. and Holanda, J.N.F. (2004). Utilization of solid waste from siderurgical industry in red ceramic. *Cerâmica*, **50:** 75-80.

Parsons, A.J., Inglethorpe, S.D.J., Morgan, D.J. and Dunham, A.C. (1997). Evolved gas analysis (EGA) of bricks clays. *J. Therm. Analysis*, **48:** 49.

Saxena, M. and Asokan, P. (2002). Timber substitute products from industrial solid wastes. *In:* Rajisnish Srivastava (ed.) Proceedings of the 18th national convention of environmental engineers and national seminar on solid waste management, Bhopal, India.

Vieira, C.M.F. and Monteiro, S.N. (2009). Incorporation of solid wastes in red ceramics: an updated review. *Matéria (Rio J.)*, **14:** 881-905.

Yalcm, N. and Sevinc, V. (2000). Utilisation of Bauxite waste in ceramic glazes. *Ceramics International*, **26:** 485-493.

Yoshizawa, S., Tanaka, M. and Shekdar, A.V. (2004). Global trends in waste generation. *In:* Gaballah, I., Mishar, B., Solozabal, R. and Tanaka, M. (eds) Recycling, waste treatment and clean technology. TMS Mineral, Metals and Materials Publishers, Madrid, Spain.

CHAPTER

21

USES OF CLAYS IN WASTE MANAGEMENTS: TOXIC AND NON-TOXIC

Methods of waste reduction, waste reuse and recycling are the preferred options when managing waste. There are many environmental benefits that can be derived from the use of these methods. They reduce or prevent green house gas emissions, reduce the release of pollutants, conserve resources, save energy and reduce the demand for waste treatment technology and landfill space. Therefore it is advisable that these methods be adopted and incorporated as part of the waste management plan. This chapter will highlight the use of clays in such processes.

21.1 INTRODUCTION

Solid waste is the unwanted or useless solid materials generated from combined residential, industrial and commercial activities in a given area. It may be categorised according to its origin (domestic, industrial, commercial, construction or institutional); according to its contents (organic material, glass, metal, plastic paper etc.); or according to hazard potential (toxic, non-toxin, flammable, radioactive, infectious etc.). Management of solid waste reduces or eliminates adverse impacts on the environment and human health and supports economic development and improved quality of life. A number of processes are involved in effectively managing waste for a municipality. These include monitoring, collection, transport, processing, recycling and disposal.

Detection of traces of toxic chemicals in drinking water supplies, in polar ice caps, groundwater sources and episodes such as those in Minamata Bay, Japan and Love Canal, USA have focused the attention of the public worldwide on the risks posed by the inappropriate disposal of hazardous waste and accidental release of toxic chemicals into the environment. In India the concern

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and need to manage the hazardous waste generated in the country in a scientific manner was felt only in the mid-eighties after the occurrence of the Bhopal gas tragedy on 2/3 December 1984. The Government's attention was then drawn towards environmental damage and the casualties that hazardous chemical substances and toxic wastes can cause. The MoEF (Ministry of Environment and Forests) enacted an umbrella act i.e., the Environment (Protection) Act in 1986. Subsequent to this Act, in order to prevent indiscriminate disposal of hazardous waste, the MoEF promulgated the Hazardous Wastes (Management and Handling) Rules in 1989, and efforts to inventorise hazardous waste generation were initiated.

Municipal solid waste consists of household wastes, construction and demolition debris, sanitation residue, and waste from streets. This garbage is generated mainly from residential and commercial complexes. There has been a significant increase in the generation of Municipal Solid Wastes (MSW) in India over the last few decades. This is largely a result of rapid population growth in the country. The daily per capita generation of municipal solid waste in India ranges from about 100 g in small towns to 500 g in large towns. The solid waste generated in Indian cities has increased from six million tonnes in 1947 to 48 million tonnes in 1997 and is expected to increase to 300 million tonnes per annum by 2047 (CPCB, 2000). The characteristics of MSW collected from any area depend on a number of factors such as food habits, cultural traditions of inhabitants, lifestyles, climate, etc. At present most of the MSW in the country is disposed off unscientifically due to lack of 'sanitary landfill'. This has adverse impacts on not only the ecosystem but also on the human environment. Unscientific disposal practices leave waste unattended at the disposal sites, which attract birds, rodents, fleas etc., to the waste and create unhygienic conditions like odour, release of airborne pathogens, etc. The plastic content of the municipal waste is picked up by the rag pickers for recycling either at primary collection centres or at dumpsites. Plastics are recycled mostly in factories, which do not have adequate technologies to process them in a safe manner. This exposes the workers to toxic fumes and unhygienic conditions. Moreover, since the rag picking sector is not organised, not all the recyclables, particularly plastic bags, get picked up and are found littered everywhere, reaching the drains and water bodies ultimately and choking them.

21.2 WASTE MANAGEMENT

Methods of waste reduction, waste reuse and recycling are the preferred options when managing waste. There are many environmental benefits that can be derived from the use of these methods. They reduce or prevent green house gas emissions, reduce the release of pollutants, conserve resources, save energy and reduce the demand for waste treatment technology and landfill space. Therefore it is advisable that these methods be adopted and incorporated as part of the waste management plan.

Methods to follow during waste management

- Waste reduction and reuse
- Recycling
- Waste collection
- Treatment and disposal
    - ➔ Thermal treatment
        - ✓ Incineration
        - ✓ Pyrolysis and gasification
        - ✓ Open burning
    - ➔ Dumps and landfills
        - ✓ Sanitary landfills
        - ✓ Controlled dumps
        - ✓ Bioreactor landfills

In this context we will only discuss about sanitary landfill to emphasise upon the use of clay in waste management.

Sanitary Landfill

Sanitary landfills are designed to greatly reduce or eliminate the risks that waste disposal may pose to the public health and environmental quality. They are usually placed in areas where land features act as natural buffers between the landfill and the environment. For example the area may be comprised of clay soil which is fairly impermeable due to its tightly packed particles, or the area may be characterised by a low water table and an absence of surface water bodies thus preventing the threat of water contamination. In addition to the strategic placement of the landfill other protective measures are incorporated into its design. The bottom and sides of landfills are lined with layers of clay or plastic to keep the liquid waste, known as leachate, from escaping into the soil. The leachate is collected and pumped to the surface for treatment. Boreholes or monitoring wells are dug in the vicinity of the landfill to monitor groundwater quality. Clay is used as an essential material for reducing the permeability of natural clay liners in landfill sites. Low porosity, slow diffusive transport, high adsorption of cations, and plasticity/swelling are among the interesting properties of clays. Some clay soils have the ability to act as membranes that restrict the passage of charged solutes. Such membrane behaviour also results in chemico-osmosis, or movement of liquid in response to a solute concentration gradient. Both these effects result in reduced solute transport through the soil barrier for waste contaminants (Saha et al., 2008).

There are certain standard values for using clays as liners materials (Corser and Cranston, 1991; Kalkana and Akbulut, 2004):

(i) The thickness of the liners varies from a few decimetres to more than 1 m depending on the waste composition.

(ii) The permeability of the soil should be less than 1 N 10^{-9} m/s for soil liners that are used for hazardous waste, municipal waste and industrial waste landfill.
(iii) The clay percentage in a given soil should be higher than 20%.
(iv) The plasticity index should be A 10 and the liquid limit should be A 30.

If these characteristics are found in a soil sample, the soil can be used as clay liner materials. However, there may be some problem using clay as liner materials.

General requirement for clay liners: The permeability of a re-molded clay is influenced by a number of factors, the key ones being plasticity, density, moisture content during compaction and method of compaction. Although the detailed requirements for compacted clay liners (CCLs) vary, the following parameters usually apply:

- Coefficient of permeability (hydraulic conductivity) of 1 × 10^{-9} m/s or less
- Minimum layer thickness of 1 m
- Minimum clay content of 10%
- Minimum fines (clay and silt) content >30%
- Plasticity index >10% and <65%
- Liquid limit <90%
- Maximum particle size of 75 mm

One major concern about clay liners is that they may be directly or indirectly attacked by the chemical wastes or leachate they are meant to contain. This interaction of metals with soil may cause the transport of heavy metals through the soil liner and result in the groundwater being contaminated (Thornton et al., 2001; Meleandez et al., 2000). Many organic and inorganic chemicals have the ability to shrink the diffuse double layer that surrounds clay particles, causing the cracking of liners, increasing the permeability of soil, with the result that the groundwater is contaminated. Changes in cation valence or electrolyte concentration of the polluted soil water account for the increase of permeability. For reactive species, some amount of solute are adsorbed by clay, but as the composition reaches a maximum, the sorbed contaminant may remain fixed to the clay or may be released if the concentration is then decreased (Rowe and Booker, 1985). The mobility of different metal ions is different depending on the size and charge of the ion particle (Roehl and Czurda, 1998; Schlegel et al., 1999). It is found that metal species do not change and the species binding rates with soil are in the order lead > copper > zinc > cadmium (Zhou, 2003). However, if some admixture materials (Broderick and Daniel, 1990), e.g., cement, lime, bentonite, gypsum, etc., are used with the soil particles for the stabilization of soil liners, the soil permeability is decreased since these materials combine with the soil, plugging the pore spaces and increasing the resistance of the soil to chemical attack. Therefore, groundwater contamination is decreased as a result.

A landfill is divided into a series of individual cells and only a few cells of the site are filled with trash at any one time. This minimizes exposure to wind and rain. The daily waste is spread and compacted to reduce the volume, a cover is then applied to reduce odours and keep out pests. When the landfill has reached its capacity it is capped with an impermeable seal which is typically composed of clay soil. Some sanitary landfills are used to recover energy. The natural anaerobic decomposition of the waste in the landfill produces landfill gases which include carbon dioxide, methane and traces of other gases. Methane can be used as an energy source to produce heat or electricity. Thus some landfills are fitted with landfill gas collection (LFG) systems to capitalise on the methane being produced. The process of generating gas is very slow, for the energy recovery system to be successful there needs to be large volumes of wastes. These landfills present the least environmental and health risk and the records kept can be a good source of information for future use in waste management. However, the cost of establishing these sanitary landfills are high when compared to the other land disposal methods.

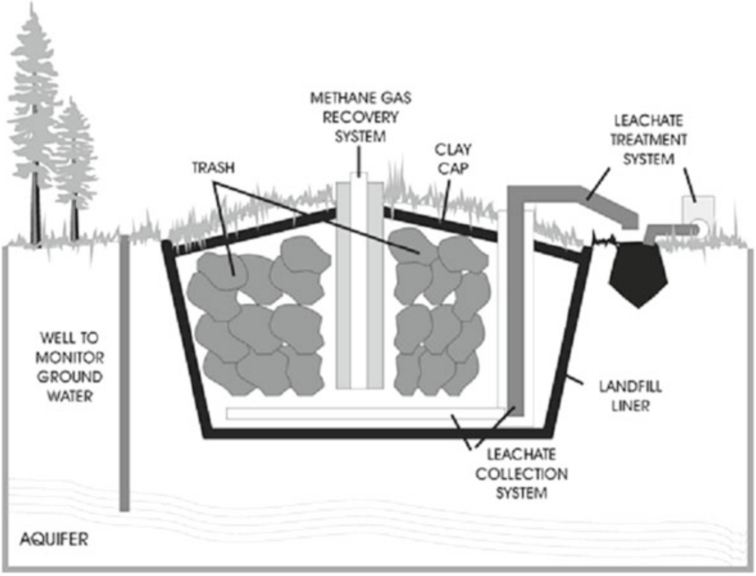

Fig. 21.1: Main features of a modern landfill.

21.3 DIFFERENT TYPES OF CLAYS IN WASTE MANAGEMENT

Use of Bentonite Clays

Clays, in particular bentonite clays, have exhibited adsorptive capacities 10 to 20 times greater than activated carbon for nonionic surfactants. Although the potential for regeneration of clays is not as plausible as for activated carbon, the mixing of clays and hazardous solid wastes prior to shallow land burial as a hazard reduction technique is still a viable alternative (Gloyna and Taylor, 1978).

Nuclear Waste Management

Radioactive wastes are perennial threats to the flora and fauna of the areas surrounding their site of disposal. Pollution from radionuclides cannot be prevented by the simple measures used for any other sort of pollutants. The environmental hazards associated to the radioactive wastes and the expensive procedures for their mitigation have frequently put into question the profitability of nuclear power production in terms of long-standing socio-economic gains. In this context, the clays are becoming gradually more and more important in the protection of environment, as it can be used effectively in some simple, less expensive procedures devised for the prevention of pollution from radionuclides. The main principle is to enclose the bodies of the radioactive wastes in a thick mass of dense, smectite-rich clays, known as a *'clay buffer'*. A brief outline of those procedures is given below.

The cylindrical masses of radioactive wastes are enclosed in containers, separated from one another by smectite-rich clays. These containers are placed in vertical boreholes or long horizontal bored or blasted tunnels. For high-level radioactive wastes, the containers are stored at a depth of 300–800 m. Low- and medium-level waste has shorter lifetimes and can be stored at smaller depth.

The preparation of buffer clay is made by compaction of dry clay powder to blocks with a high density. The blocks are then placed in the deposition holes to surround the containers. Very dense blocks of highly compacted smectitic clay powder are placed around the containers, embedding them tightly. The required tightness is attained when the clay material swells after taking up water from the surrounding rock.

The raw bentonite is so uniform and rich in smectite that only simple drying in the sun of the excavated material with subsequent grinding is required at the quarries and plants. However, in most cases the clay material must be dried in rotating kilns, and also transformed to a suitable Na^+-rich form.

The following properties of smectite-rich clays make them suitable for this purpose:

(i) Very low hydraulic conductivity
(ii) Low anion diffusion capacity and low transport capacity of positively charged radionuclides
(iii) A high swelling potential for self-sealing of gaps and openings in the buffer and its contacts with the rock and containers
(iv) Favourable rheological properties, such as sufficient bearing capacity to minimise settlement of the heavy containers, and sufficient softness to avoid transfer of high tectonically induced shear stresses to the containers

(v) Sufficient thermal conductivity to transfer heat caused by the radioactive decay to the rock without being too hot

Extensive research work has been going on for the safe disposal of radioactive wastes in different parts of the world, especially in the North American and West European countries where fission reactors are aplenty. Different types of clays and clay-derivatives are found to be more effective in safe disposal of different types of radioactive wastes. The clays are easily available than any other buffer materials, and the procedures of waste disposal with clay buffer are less expensive. This encourages the researchers to explore further possibilities of application of clays in this field.

Experiment 1: Where feasible to handle as part of the regular management programme, dry droppings under cages in open houses are the most satisfactory method of solving the waste utilization problem. Dehydration of the droppings and water removal from environmentally controlled laying houses are problems of major concern to those engaged in the commercial egg business. Water consumption and excretion rates are under partial genetic control. In 1962-64, certain commercial strains of laying birds were experiencing difficulty with wet droppings. A solution was sought with dietary bentonites. Diets with 2.5 and 5 per cent western bentonite were used. Percentage of moisture in the droppings was significantly ($P < 0.05$) reduced in both winter and summer seasons and the consistency so changed that drying was speeded up. Performance data on the birds were also collected. Body weight and egg size were significantly ($P < 0.05$) increased although the caloric value of the diets decreased from 945 kcal of productive energy per pound for the control to 932 and 918 for the 2.5 and 5 per cent bentonite diets, respectively. There was no significant effect on egg production but feed efficiency was improved.

That less feed is required per unit of eggs produced on lower calorie diets substantiates the conclusion that the betonites improved caloric efficiency. These and other data presented in this study assured the breeder involved and cage operators in general that sodium bentonite offered real promise for control of wet droppings and that it might also be of value to operators of environmentally controlled houses (Quisenberry, 1968).

Experiment 2: For this experiment, calcium bentonite from a Texas source and a sodium bentonite from a western source were compared. The bentonites were fed at the five per cent level only. As for Experiment l, the control diet contained 945 kcal of productive energy and the bentonite diets contained only 918 kcal/lb. Birds that received the bentonite diets gained more body weight and produced larger eggs than the controls. Thirteen per cent more commercially designated "large" eggs were produced by birds on the calcium bentonite diet and 15 per cent more by the sodium bentonite group. Egg production was higher for the bentonite group, particularly for those on the western bentonite. Mortality was also lower than for the controls. Feed efficiency, however, favoured the controls in this experiment, in contrast to Experiment 1 (Quisenberry, 1968).

Experiment 3: Encouraged by results of the first two experiments, a third one was devised to test the efficacy of two montmorillonite clays, one from California (Cal-Min) and one from Texas (BMC), calcium bentonite from a Texas source and a western bentonite supplied by the Magnet Cove Barium Corporation, Houston, Texas. Each of these was fed at two and five per cent levels. As for Experiment 1, all of the clay additives at both levels resulted in a significant ($P < 0.05$) gain in body weight over the controls, an increase in egg size, and a reduction in water of the droppings. Egg production was improved by the cal-min, the lower level of BMC, and both levels of western bentonite. Feed efficiency was measurably improved by the 2.5 per cent level of cal-min and slightly improved by the higher level of cal-min and the lower level of western bentonite. The other additives were no better or poorer than the controls. The value of these clays and bentonites in assistance with the solution of wet droppings problem was again demonstrated (Quisenberry, 1968).

Kaolinite

Kaolinite is the most common mineral in this group and consists of stacks of 1:1 unit cells comprised of silica tetrahedral and gibbsite (Al) octahedral sheets. The stacks generally range from 0.05 to 2 μm in thickness and can attain thicknesses up to 4000 μm; the stacks can range from 0.1 to 4 μm laterally. The specific surface area of kaolinite is of the order of 10 to 20 m^2/g of dry clay.

A small net negative charge on kaolinite particles results in a cation exchange capacity of 3 to 15 meq/100 g. This charge has been attributed to a small amount of isomorphous substitution in the silica or gibbsite sheets, replacement of exposed hydroxyl hydrogens by exchangeable cations, broken bonds around particle edges, or diffuse charges resulting from the large size and surface accessibility of O^{-2} and OH^- molecules (Mitchell, 1976; Winterkorn and Fang, 1975). The stacked crystal structure of kaolinite results in a blocky form for this clay mineral and a larger size and lower surface-to-volume ratio than other clay minerals. This low surface area, combined with the relatively small negative surface charge, results in kaolinite being the least electrochemically active and least plastic clay mineral.

Because of the blocky structure of kaolinite particles, crystal edges of this mineral group comprise 10 to 20 per cent of the total crystal area (Theng, 1974) and therefore exert a stronger influence on the electrochemical behaviour of these minerals than do the crystal edges of smectites or illites (crystal edges comprise 2 to 3 per cent of total crystal area for montmorillonite; Theng, 1974). Broken bonds on these edges result in unsatisfied valences that can be satisfied by cation or anion adsorption. However, unlike the structurally generated negative charges on the platy crystal surfaces, these charges are affected by the pH of the environment. Evidence suggests that the edges are positively charged at low pH and negatively charged at high pH. This results in kaolinite having a low cation exchange capacity at low pH and higher cation exchange capacity at high pH. Kaolinite has a higher anion exchange capacity than most clay minerals. This may result from the presence of replaceable hydroxyl ions on the outside of structural sheets. Kaolinite thus has the ability to fix certain negative ions (Deer et al., 1966).

Compared with other clay minerals, kaolinite has a lower affinity for water, has a lower dispersivity, and does not achieve as low a permeability upon compaction. On the other hand, because it is not as electrochemically active, its behaviour may be less affected by chemicals than other clay minerals. Thus, a kaolinitic clay liner may have a higher permeability than liners composed of other clays, but the permeability of a kaolinitic clay liner may not be as sensitive to changes in moisture content or to chemical attack.

Halloysite

Halloysite is another kaolinite group mineral that is a common soil constituent in some areas. This mineral occurs in two forms: a nonhydrated type with a structural composition similar to kaolinite and a hydrated form with a single layer of water interposed between unit kaolinite layers. This layer increases the basal spacing to 10.1 Angstrom, compared with 7.2 Angstrom for non-hydrated halloysite and kaolinite. Partially hydrated halloysite (metahalloysite) with basal spacing from 7.4 to 7.9 Angstrom can also occur. The interlayer water molecules in hydrated halloysite are believed to be in a rather flat hexagonal network linked to each other and to adjacent halloysite layers by hydrogen bonding.

The hydrated form of halloysite occurs in cylindrical tubes of overlapping kaolinite sheets. The outside diameters of the tubes range from 0.05 to 0.20 μm, with a median value of 0.07 μm, and range in length from a fraction to several micrometres. The specific surface area of halloysite ranges from 35 to 70 m^2/g (Mitchell, 1976).

Because of the interlayer water sheet in hydrated halloysite, intercalation (introduction between the unit cells) of chemicals can occur. This also results in a slightly higher cation exchange capacity for hydrated halloysite (5 to 40 meq/100 g) than for kaolinite (3 to 15 meq/100 g). Halloysite also may be more affected by chemicals than kaolinite.

The interlayer water in halloysite is easily removed during drying, and this dehydration is irreversible. Because of this phenomenon, soil engineering tests on air-dried samples can give different results than those performed on samples at the original field moisture content. For this reason, it is especially important that laboratory tests on soils with appreciable halloysite content be carried out on samples at the original field moisture content (Holtz and Kovacs, 1981; Hilf, 1975).

Illite

Illite is an important constituent of clay soils and has been described by Mitchell (1976) as "perhaps the most commonly occurring clay mineral found in soils encountered in engineering practice." Illite has almost the same crystalline structure as muscovite mica. This structure is comprised of a silica-gibbsite-silica sandwich, with the tips of the silica tetrahedra pointing towards the octahedral gibbsite sheet and the oxygens at the tips being common with the octahedral sheet. Isomorphous substitution of aluminium for silicon in the tetrahedral sheet results in a negative charge at the surface of these layers. This charge is balanced by potassium, cesium and ammonium ions between the 2:1 layers; these ions fit tightly in the 1.32-Angstrom-radius holes in the bases of the silica sheet and as a result are fixed in position and are not exchangeable. Illite differs from muscovite in having less isomorphous substitution in the tetrahedral sheet, a lower negative surface charge, and a lower amount of potassium between the layers. The stacking of illite layers is also more random, and illite occurs with a much smaller particle size than muscovite. In terms of properties important to clay liner performance, illite lies between kaolinite and the smectite clay minerals. Although extensive isomorphous substitution results in a net negative charge on the clay mineral surface, the fixed potassium cations balance the charges and strongly bond adjacent 2:1 sheets together. As a result, illite has intermediate values for surface area (65 to 100 m^2/g), cation exchange capacity (10 to 40 meq/100 g), swelling index, and activity. It is also intermediate in its reaction to chemicals. Because of the strength of the interlayer potassium bonding, the basal spacing of illite remains at 10 Angstrom when it is exposed to polar liquids (Mitchell, 1976). The potassium ions effectively prevent the intercalation of water, organic liquids, and other cations (Deer et al., 1966).

Vermiculite

Vermiculite is a fairly common mineral in clay soils and usually occurs with other clay minerals. Vermiculite has a 2:1 structure with a poorly organized octahedral sheet sandwiched between two silica tetrahedral sheets. The octahedral sheet contains iron and magnesium ions. As with illite, isomorphous substitution of aluminium for silicon is extensive in the tetrahedral sheet, resulting in a net negative charge on the crystal surface. This positive charge deficiency is larger than that of the smectite minerals and is usually balanced by interlayer layers of divalent cations and water. This larger charge deficiency results in vermiculite having the highest cation exchange capacity of all clay minerals (Deer et al., 1966). The most common interlayer cations in vermiculite are magnesium and, to a lesser extent, calcium. The amount of water that is intercalated in vermiculite is less variable than that in smectite and usually is limited to two layers of water molecules. The interlayer spacing is therefore fairly constant for vermiculite but varies to some extent depending on the cations present between the layers. Vermiculites can absorb organic liquids between their layers but take up less than the smectite minerals (Deer et al., 1966). The primary specific surface area for vermiculite ranges from 65 to 100 m^2/g. This is within the range reported for montmorillonite and, as with montmorillonite, the secondary (interlayer) surface area can reach very high values (870 m^2/g) (Mitchell, 1976).

21.4 WASTE MANAGEMENT: TOXIC

Jarosite poses serious problem for disposal due to release of toxic elements, which ultimately contaminate the soil, ground water, aquatic life and human health. Results revealed from the present study that the compressive strength of jarosite products attained as high as 140.8 ± 1.85 kg/cm^2 and the water absorption capacity is 14.51 ± 0.50% at the combination of 3:1 ratio of jarosite and clay, respectively, but, shrinkage was higher (31.36 ± 1.00%) and toxic elements were not under safe limit. Results revealed that during sintering process under solid-state reaction, toxic substances/elements in jarosite were detoxified/immobilised through complexing in the silicate matrix. During firing of jarosite bricks, a considerable amount of liquid phase formed might have reduced the porosity and specific surface area under the capillary tension forces in the fine pores of the s/s jarosite-sintered products resulting in less water absorption and higher compressive strength. This could be attained by the mineralogical changes/phase transformation due to firing the s/s products at 960 ± 2°C and further this was confirmed from the SEM microstructure of the fracture surface. It was confirmed that the leaching potentials of toxic elements such as Pb, Cd, Cr, As, Se, Ag and Ni in s/s-sintered products developed using 1:1, 2:1 and 3:1 jarosite clay ratios with 15–30% fly ash were below the concentration of USEPA–TCLP standard. However, the optimum mix design of 2:1 with 15% fly ash was found to be the intermediate condition to have both satisfactory compressive strength of 45.63 ± 0.88 kg/cm^2 with shrinkage of 12.24 ± 0.59% in which toxic elements concentration was below safe limits and has the potential to use in construction applications as walling materials. The outcome of the study is expected to result in as one of the major solutions for safely recycling the hazardous jarosite released from zinc industries in developing non-hazardous products which can ultimately be used in building applications.

Municipal solid waste disposal in the landfill is the most common solid waste management practice followed throughout the world. However, landfill requires a close environmental engineering surveillance in its design and operation, as it is likely to generate leachate, which would potentially contaminate nearby ground water and surface water. With the changing nature of domestic refuse composition over the years, the proportion of refuses available for decomposition has greatly increased and thus the organic strength of the leachate, resulting in its greater potential for pollution.

Landfill leachate can broadly be defined as the liquid produced from the decomposition of waste and infiltration of rainwater in the landfill. Generation of leachate occurs when moisture enters the refuse in a landfill, dissolves the contaminants into liquid phase and becomes sufficient to initiate a liquid flow. Leachate varies from one landfill to another with fluctuations that depend on short and long term due to variations in climate, hydrogeology and waste composition.

Among the different pollutants occurring in leachate, heavy metal ions are the most toxic inorganic polluants which occur in soils and can be of natural or of anthropogenic origin.

Heavy metals present in the form of free cations or in labile complexes (which can easily dissociate) will generally have a more harmful effect on aquatic organisms than metal in non-labile complexes, since the free metal form is both very mobile and can easily absorb onto, or pass into, the tissue of marine organisms.

The literature reports that typically less than 10% of metals in landfill leachate are present as free metal ions. Depending on the leachate characteristics, various techniques can be used to treat this hazardous wastewater (e.g. biological treatments, physico-chemical treatments, such as chemical precipitation, ion exchange, adsorption). Among these treatments, adsorption techniques have proven successful in removing heavy metals.

A hazardous waste landfill is designed to receive wastes that are potentially harmful if improperly handled (Fig. 21.2).

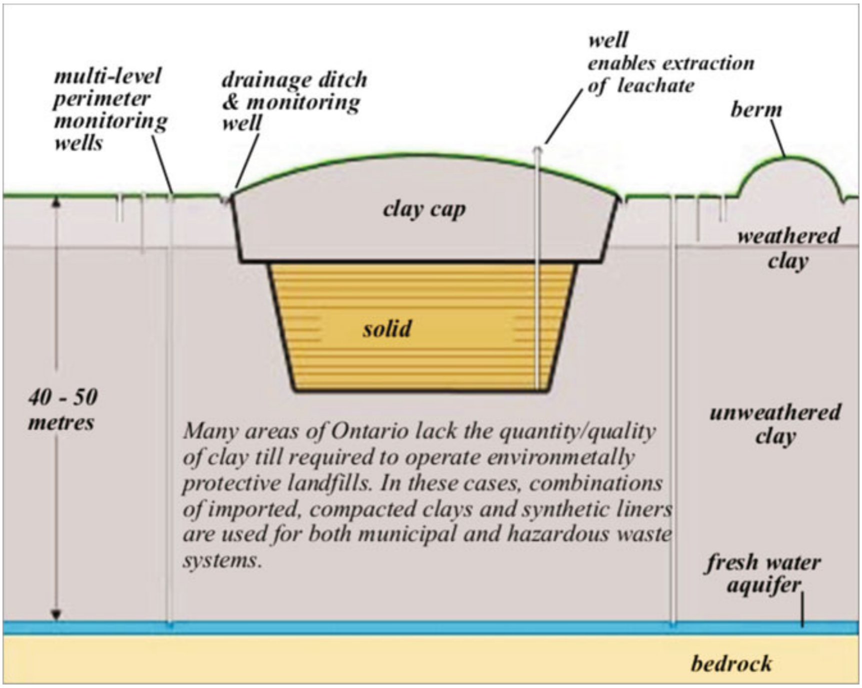

Fig. 21.2: Cross section of a closed secure landfill cell.

Landfill design addresses the need to protect both surface and ground water. Waste is deposited in the unweathered clay and then capped with compacted clay. An extension of this cap into the unweathered clay makes construction of cut-off walls (shown in Fig. 21.2) unnecessary. A network of multi-level monitoring wells makes possible the sampling of ground waters—a check to ensure that wastes are being contained. Leachate formed by rainfall and/or snow melt is removed and treated by high-temperature incineration.

Activated carbon has been the most widely used adsorbent because of its high capacity for the adsorption of heavy metals. However, due to the difficulty and expense involved in regeneration, clays are being considered as alternative low cost adsorbents (Weng and Pan, 2007; Tahir and Rauf, 2006; Wolfe et al., 1985). Studies show that the adsorption capabilities of clays are due to a net negative charge on the silicate minerals which is neutralized by the adsorption of positively charged cations such as cationic dyes, heavy metals etc. The other main reason for the high adsorption capacity of clays is the large surface areas ranging up to 800 $m^2.g^{-1}$.

Clay minerals, mainly montmorillonite, play an important role in this remedial treatment of hazardous waste. The ions on the surface of clay particles may be O^{2-} or OH^-, which give the clay particle a net negative electric charge. The negative electric charge is balanced by the external adsorption of cations at the surface of particle and between the sheets. These externally absorbed cations can be replaced by other cations, which is also the ion-exchange. In the case of montmorillonite, it is well known that the crystal consists of an aluminium sheet between two silica sheets, i.e. a 2:1 mineral. The bond holding sheets is due to Van der Waals forces and exchangeable ions. It is very weak bond and easily broken by water or other polar or cationic organic fluids entering between the sheets. There is extensive substitution of silica and alumina, resulting in considerable charge deficiency, which results in high cation exchange capacity.

Poorly crystalline clay minerals such as allophanes also play a vital role in the treatment. They are formed from weathering process of volcanic ash under poor drainage conditions and/or humid climate. Weathering products of volcanic ash are widely distributed in Japanese island arc and one of the typical deposits is named as the “Kanto Loam”. Similar products containing poorly crystalline clay minerals are expected from weathered granite, named as “Masado”. In our remedial treatment, the poorly crystalline clay minerals, or even amorphous silicate, show anion exchange capacity and further crystallization which integrate existing toxic cations into the crystal structure as a trace element (Minato and Shibue, 1999).

21.5 WASTE MANAGEMENT: NON-TOXIC

The most economic and most commonly used tailings deposition technique is wet deposition near the mine site. In this technique, water-sediment slurry is pumped in nearby topographic depressions, lakes or drainage basins. An also often economic practice was sea deposition, when the mine was located close to the ocean, with sometime hazardous effects on the environment (Dold, 2006). Other techniques are a semi-dry sub-aerial method, thickened discharge, and deep-water disposal (Ritcey, 1989). In countries with pronounced topography (e.g., Chile), most of the tailings impoundments are designed as valley dam impoundments. This type of design is provided by placing an embankment across the valley at the head end of drainage. The most common dam construction methods are the downstream and upstream methods. In the wet deposition method, the tailings slurry is thickened to 35-40% solids and discharged by either point or line discharge. Often a discharge point is moved periodically. As a result of a periodical move of the discharge point and gravimetrical grain size separation occurring in the tailings, a general trend of coarser to finer grain size from the tailings discharge point to the pond can be observed. Additionally, inhomogeneous layering of fine sand with silt and clay horizons makes the hydrological situation in the tailings material very complex. In general, it must be assumed that the coarser horizons are responsible for permeability, and that they behave as connected aquifers. This should be taken into account in sampling and the calculation of permeability coefficients. As the horizons have thickness in the range of centimetres to decimetres, frequently, bulk samples lead to too low permeability coefficients.

The acid produced in the processes presented above may result normally in pH in the range of 1.5-4 in the mine waste environment. Exceptionally, pH can reach even negative values (Nordstrom et al., 2000). This acidity together with Fe(III) is able to dissolve minerals and mobilize elements in the tailings (Dold and Fontboté, 2001). In their pathway, the acid produced and the elements mobilized react with acid-neutralizing minerals such as carbonates or silicates. Acid-neutralizing reactions result in an increase in the pore-water pH. This increase in pH is frequently accompanied by precipitation of metal-bearing oxyhydroxide and oxyhydroxide sulphate minerals that remove dissolved metals from the water migrating within the tailings pore space. These secondary minerals act in a certain pH range as buffers so that a sequence of pH buffering reactions can be observed in the tailings environment (Blowes and Ptacek, 1994).

Dissolution of most aluminosilicate minerals also consumes H^+ ions and contributes base cations (Ca, Mg, Fe(II)), alkali elements (Na, K) and dissolved Si and Al to the tailings pore water (Blowes and Ptacek, 1994). Though, dissolution of aluminosilicate minerals is slower than of metal hydroxides and much slower than that of carbonates. Feldspar weathering is mainly controlled by pH, silica, Na, K and Ca concentrations. One possible reactions path is:

$$\text{K-feldspar} \geq \text{kaolinite} \geq \text{gibbsite}$$

Reactions (1) and (2) illustrate this path.

$$\underset{\text{K-feldspar}}{2KAlSi_3O_8} + 9H_2O + 2H^+ \longrightarrow \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 2K^+ + 4H_4SiO_4 \qquad (1)$$

In this reaction, K and Si enter the solution, while protons are consumed. The solubility of feldspar increases when proton activity increases or the removal of K or Si is fast, e.g. by secondary mineral formation. Secondary kaolinite may dissolve to form gibbsite, a reaction that does not neutralize acid:

$$\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 5H_2O \longrightarrow \underset{\text{gibbsite}}{2Al(OH)_3} + 2H_4SiO_4 \quad (2)$$

Higher pH and K concentrations can lead theoretically to muscovite formation instead of kaolinite as secondary mineral of feldspar weathering:

$$\underset{\text{K-feldspar}}{3KAlSiO_3O_8} + 12H_2O + 2H^+ \longrightarrow \underset{\text{muscovite}}{KAl_2(AlSi_3O_{10})(OH)_2} + 2K^+ + 6H_4SiO_4 \quad (3)$$

and muscovite reacts forming gibbsite:

$$\underset{\text{muscovite}}{KAl_2(AlSi_3O_{10})(OH)_2} + 9H_2O + H^+ \longrightarrow \underset{\text{gibbsite}}{2Al(OH)_3} + 3H_4SiO_4 + K^+ \quad (4)$$

However, these reactions have to be seen as a strong simplification of the very complex clay mineral group and their formation processes. In the case of plagioclase, the weathering path is similar to that of K-feldspar and is accompanied by the release of sodium and/or calcium. Under low pH conditions plagioclase will react to form kaolinite, while under higher pH smectite will be formed.

Nesbitt and Jambor (1998) have shown the fundamental role of mafic minerals in neutralization of the Waite-Amulet tailings. As in the weathering of feldspar, the weathering of felsic minerals leads to the formation of clay minerals. Muscovite, pyroxene and amphibole alter to chlorite. By decreasing pH, chlorite alters to sericite, kaolinite or Mg-montmorillonite. The products of biotite alteration are hydrobiotite, a regularly interstratified biotite-vermiculite phase, vermiculite, and kaolinite (Acker and Bricker, 1992; Malmström and Banwart, 1997). Direct conversion of biotite to kaolinite has also been described (Acker and Bricker, 1992).

Concluding Remarks

This chapter enables us to get acquainted with the various applications of clays in waste management related to both toxic and non-toxic substances.

QUESTIONS

1. What do you mean by toxic and non-toxic wastes? How clays can be related to their management?
2. What are the properties of clay required to use them as landfills?
3. All types of clays cannot be used in management of both toxic and non-toxic wastes. Show with a chart the waste management by various types of clays stating their properties.

4. 'Kaolinite has a higher anion exchange capacity than most clay minerals.' Show how this property can be used in waste management.
5. How can the cation-exchange capacity of different types of clays be used in waste management?
6. What are the steps generally followed in toxic and non-toxic waste management? State individually.
7. How can the weathering process be related to the waste management by clay minerals?
8. What do you mean by the term 'leachate'? What is its role in landfill operations?

FURTHER READING

Acker, J.G. and Bricker, O.P. (1992). The influence of pH on biotite dissolution and alteration kinetics at low temperature. *Geochimi ca et Cosmochimica Acta.*, **56:** 3073-3092.

Blowes, D.W. and Ptacek, C.J. (1994). Acid-neutralization mechanisms in inactive mine tailings. *In:* J.L. Jambor and D.W. Blowes (eds), Short course handbook on environmental geochemistry of sulfide mine-waste. Mineralogical Association of Canada, Nepean.

Broderick, G.P. and Daniel, D.E. (1990). Stabilizing Compacted Clay against Chemical Attack. *J. Geotech. Eng. ASCE*, **116(10):** 1549.

Corser, P. and Cranston, M. (1991). Observations on the Performance of Composite Clay Liners and Covers. Proc. Geosynthetic Design and Performance, Vancouver Geotechnical Society, B.C.

Dold, B. (2006). Element flows associated with marine shore mine tailings deposits. *Environmental Science and Technology*, **40:** 752-758.

Dold, B. and Fontboté, L. (2001). Element cycling and secondary mineralogy in porphyry copper tailings as a function of climate, primary mineralogy, and mineral processing. *In:* Special Issue: Geochemical studies of Mining and the Environment. *Journal of Geochemical Exploration*, **74(13):** 3-55.

Gloyna, E.F. and Taylor, R.D. (1978). Elimination of the Hazards from Hazardous Wastes. *Environmental Health Perspectives*, **27:** 323-335.

Kalkana, E. and Akbulut, S. (2004). The Positive Effects of Silica Fume on the Permeability, Swelling Pressure and Compressive Strength of Natural Clay Liners. *Eng . Geol.*, **73:** 145.

Malmström, M. and Banwart, S. (1997). Biotite dissolution at 25°C, the pH dependence of dissolution rate and stoichometry. *Geochimica et Cosmochimica Acta*, **61:** 2779-2799.

Meleandez, G.M., Korre, A. and Parry, S.J. (2000). Influence of Soil pH on the Fractionation of Cr, Cu and Zn in Solid Phases from a Landfill Site. *Environ. Pollut*. (Amsterdam, Neth.), **109:** 497.

Minato, H. and Shibue, Y. (1999). A case for utilization of clays to raw materials of outside wall at final disposal site of town waste matters and new treatment techniques for pollution soils. *Clay Science* (Nendo Kagaku), **38:** 167-180.

Nesbitt, H.W. and Jambor, J.L. (1998). Role of mafic minerals in neutralizing ARD, demonstrated using a chemical weathering methodology. *In:* L.J. Cabri and D.J. Vaughan (eds), Modern approaches to ore and environmental mineralogy, Mineralogical Association of Canada.

Nordstrom, D.K., Alpers, C.N., Ptacek, C.J. and Blowes, D.W. (2000). Negative pH and extremely acidic mine waters from Iron Mountain, California. *Environ. Sci. Technol.*, **34:** 254-258.

Quisenberry, J.H. (1968). The use of clay in poultry feed. *Clays and Clay Minerals*, **16:** 267-270.

Ritcey, G.M. (1989). Tailings management, problems and solutions in the mining industry. Elsevier, Amsterdam.

Roehl, K.E. and Czurda, K. (1998). Diffusion and Solid Speciation of Cd and Pb in Clay Liners. *Appl . Clay Sci.*, **12:** 387.

Rowe, K.R. and Booker, J.R. (1985). 1-D Pollutant Migration in Soils of Finite Depth. *J. Geotech . Eng . ASCE*, **111(4):** 479.

Saha, P., Datta, S. and Sanyal, S.K. (2008). Hazardous Waste Pollution Prevention Using Clay with Admixtures. *Clean*, **36(2):** 230-238.

Schlegel, M.L., Charlet, L. and Manceau, A. (1999). Sorption of Metal Ions on Clay Minerals. *J. Colloid Interface Sci.*, **220:** 392.

Tahir, S.S. and N. Rauf (2006). Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay. *Chemosphere*, **63:** 1842-1848.

Thornton, S.F., Lerner, D.N. and Tellam, J.H. (2001). Attenuation of Landfill Leachate by Clay Liner Materials in Laboratory Columns. *Waste Manage. Res.*, **19:** 70.

Weng, C.H. and Pan, Y.F. (2007). Adsorption of a cationic dye (methylene blue) onto spent activated clay. *Journal of Hazardous Materials*, **144:** 355-362.

Wolfe, T.A., Demirel, T. and Bauman, E.S. (1985). Interaction of aliphatic amines with montmorillonite to enhance adsorption of organic pollutants. *Clays Minerals*, **33:** 301-311.

Zhou, P. (2003). Clay Landfill Liners Subject to Variable Interfacial Redox and pH conditions – Heavy Metal and Clay Interactions. Ph.D. Thesis, Louisiana State University.

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S. Mukherjee, *The Science of Clays: Applications in Industry, Engineering and Environment*,
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