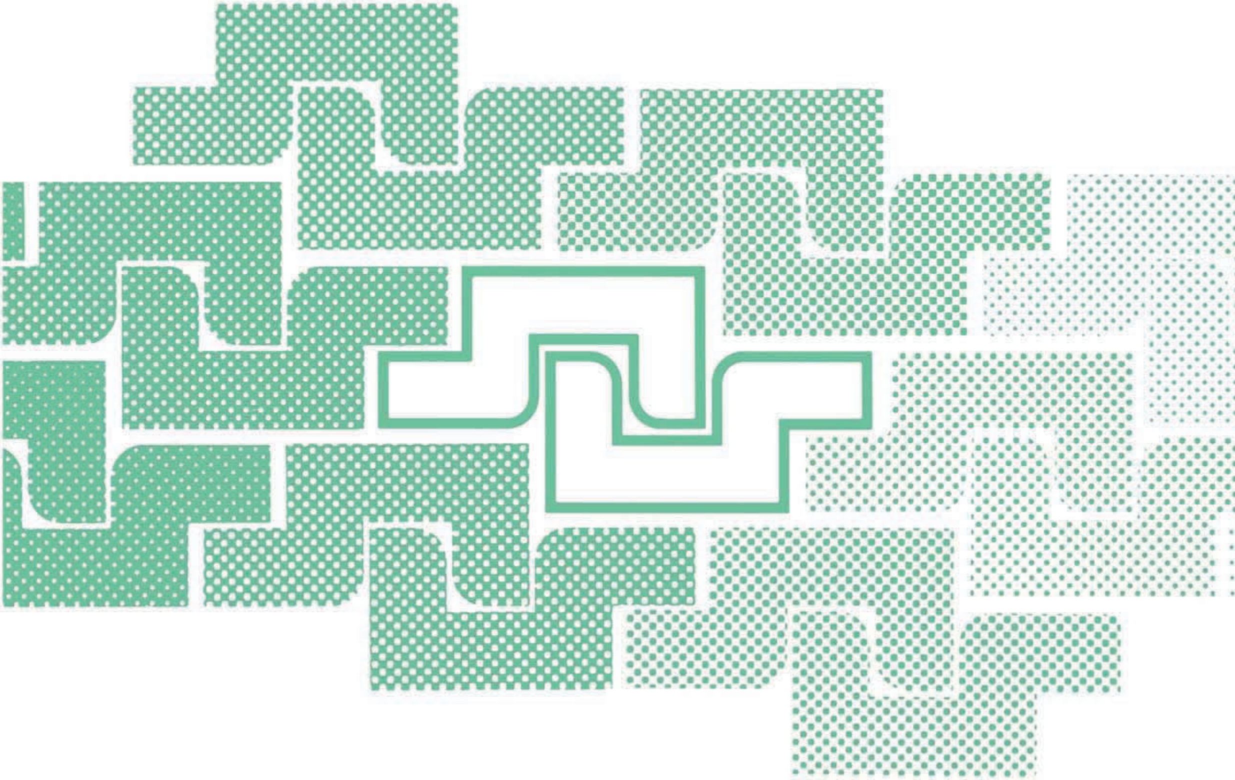

Modern Tools and Methods of Water Treatment for Improving Living Standards

Edited by

Alexander Omelchenko,
Alexander A. Pivovarov and W. Jim Swindall

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IV. Earth and Environmental Sciences – Vol. 48

Modern Tools and Methods of Water Treatment for Improving Living Standards

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IV. Management of Water Resources, Planning, Training and Education in Water Treatment

PREFACE

Providing the population of the Earth with safe drinking water is one of the biggest challenges of modern society. In recognition of this problem the United Nations Organization and UNESCO declared 2003 to be the International Year of Freshwater.

On November 19-22, 2003, the NATO Advanced Research Workshop (ARW) on “Modern Tools and Methods of Water Treatment for Improving Living Standards” took place in Dnepropetrovsk, Ukraine. Thirty-one participants from 15 countries including Bulgaria, Canada, Croatia, Czech Republic, Denmark, Italy, Lithuania, Moldova, Poland, Romania, Russia, UK, Ukraine, USA, and Uzbekistan attended the meeting. They discussed the scientific concepts and practical means for the solution of the complex social, economic and ecological problems associated with water purification, consumption, conservation, and protection. They also established a network of scientists and specialists to foster further collaboration and the exchange of ideas.

The location of the ARW was chosen quite deliberately. The city of Dnepropetrovsk is located on the banks of the Dnieper River and it has a population of about 1.3 million people. As it is one of the largest industrial centers, it shares all the environmental problems, which are found in the modern Ukraine. In 2001, one in seven of the water samples taken from Ukrainian industrial and drinking water supply systems did not meet sanitary-hygienic standards, and one in twelve did not meet microbiological standards. Water analyses conducted during 2000 in the two largest Ukrainian cities, Kiev and Kharkiv, showed that all water samples exhibited some level of toxicity. Chemical pollution and microbial contamination of drinking water significantly reduces the living standards of the population. The quality of drinking water is considered to be a component of national safety of Ukraine.

The Research Workshop was divided into four sessions. In session 1 “Recent Advances in Purification and Special Treatment of Water and Water Quality Monitoring”, participants were acquainted with recent advances in drinking water treatment in the United States, biological control in water-cooling towers in the United Kingdom, and the use of radionuclides Pb-210 and Cs-137 for monitoring contamination in the Canadian Arctic. Three presentations were dedicated to the use of biosensors and mobile analytical tests for water quality monitoring and methods of rapid detection of bacteria in drinking water. In Session 2 “Development of Modern Technologies of Special Water Treatment for Use in Various Areas of Science, Industry and Public Health”, some innovative methods and tools, such as electrochemically-stimulated sorption and sorption-membrane methods, a bubble-extraction method, fibroid sorbents, in-situ oxygen curtain technology, ion-exchange membranes, electrochemically-generated silver and copper ions and colloidal gold for water purification and post-purification were presented. In session 3 “Tools and Methods for Achievement of High Technological Parameters of Water Purification and Wastewater Treatment”, studies into the treatment of wastewaters were discussed. Among them were water reclamation and recycling in Danish industry, biocide polymers as a new opportunity in water treatment, optimization of galvanic wastewater treatment processes, efficiency of nitrification and denitrification processes in wastewater treatment plants, electrochemical processes for wastewater purification employing fluidized beds of particles, cold plasma as a new tool for purification of wastewater from chemical contaminants, bacteria and viruses. In Session 4 “Management of Water Resources, Planning, Training and Education in Water Treatment”, management of water resources in the United Kingdom, Bulgaria, Poland, Croatia, and Romania using a variety of case studies were presented. The important issue of industry-university cooperation for postgraduate education and training in the water treatment area was also discussed.

All of the above subjects are covered in this book. We believe that this book will be helpful to the international community of scientists, specialists and students dealing with water treatment, purification, conservation and protection.

Only the formal presentations are included in this book. Unfortunately all the heated discussions, exchange of information and informal gatherings could not be reflected in it. The meeting resulted in the creation of a network, collaborative links, and personal friendships between scientists and specialists from NATO and Partner countries, which extends the positive outcome of the meeting far beyond its boundaries.

This meeting would not have been successful without students-volunteers from the Ukrainian State Chemical Technology University, Dnepropetrovsk: Tatyana Bolva, Boris Dubina, Oksana Holovko, Dmitri Misnyankin, Dmitri Pshinnik, Andriy Reshetnikov, and Natalia Vedyakina, and their leader Dr. Anna P. Tischenko. The essential help from Dr. Naranjan S. Dhalla and Mr. Ivan Berkowitz from the International Academy of Cardiovascular Sciences, and Dr. John Foerster from St. Boniface General Hospital Research Centre is greatly appreciated. We would also like to express our sincere gratitude to Dr. Alain H. Jubier, Programme Director, Environmental Security, NATO, and to his administrative assistant Ms. Lynn Campbell-Nolan. Special thanks should be addressed to Ms. Annelies Kersbergen from the NATO Publishing Unit of Kluwer Academic Publishers for her constant interest, guidance, and great patience.

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PART I

RECENT ADVANCES IN PURIFICATION AND SPECIAL TREATMENT OF WATER AND WATER QUALITY MONITORING

ADVANCES IN DRINKING WATER TREATMENT IN THE UNITED STATES

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ABSTRACT

The United States drinking water public health protection goal is to provide water that meets all health-based standards to ninety-five percent of the population served by public drinking water supplies by 2005. In 2002, the level of compliance with some eighty-five health-based standards was ninety-four percent. This significant accomplishment has been achieved through strong regulation and technical support to drinking water supply systems. The engineering and risk management research program that supports drinking water regulation has developed the Drinking Water Contaminant Management Framework to organize research related to control of a contaminant or group of contaminants in drinking water. The recent lowering of the arsenic drinking water standard serves as a case study for application of the Framework. Emerging research areas include the use of DNA based analytical techniques to advance our understanding of microbial contaminants in drinking water and water security. Real-time monitoring techniques will require significant advancement before they can be relied upon to insure drinking water protection.

INTRODUCTION

The United States remains strongly committed to providing safe drinking water for all of its citizens. This policy is codified in the Federal Safe Drinking Water Act. The United States Environmental Protection Agency (EPA) is responsible for insuring compliance with this law. The national goal for drinking water is to provide water that meets all health-based standards to ninety-five percent of the population served by public drinking water supplies by 2005 (U.S. EPA, 1999). Public water supply systems are, by definition for community settings, those that serve fifteen connections or twenty-five people at least sixty days out of the year. At the present time, there are some eighty-five health based microbial, radionuclide and chemical drinking water standards in effect. In 2002, the level of compliance with these health-based

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standards was ninety-four percent (U.S. EPA, 2003). This significant accomplishment has been achieved through strong regulation and technical support, over the last twenty-nine years, to the 170,000 drinking water supply systems that serve more than 260 million consumers.

This paper will discuss the research approach to control contaminants in drinking water that includes source water protection, add-on treatment, distribution system effects and residuals management; apply the research approach to the newly promulgated standard for arsenic in drinking water; discuss recent advancements in distribution system biofilm characterization and outline priority research regarding water system security.

DRINKING WATER CONTAMINANT MANAGEMENT FRAMEWORK

A key element to the success of the drinking water protection program has been a sustained research effort to provide control methods and engineering technology to help water systems comply with the regulations. The Water Supply and Water Resources Division of EPA's Office of Research and Development, National Risk Management Research Laboratory based in Cincinnati, Ohio has provided this critical research support.

Recently, the Division has established a conceptual model to identify research gaps for any contaminant or group of contaminants that need to be controlled in drinking water. This approach is termed the Drinking Water Contaminant Management Framework (Schmelling and Gutierrez 2002). The Framework identifies four points that must be considered in the development of a control strategy: (1) source water protection, (2) add-on treatment, (3) distribution system effects, and (4) residuals management. Results from studies and evaluations of the four control points then feed into cost-effectiveness determinations to develop sets of acceptable control options. It is important to note that not every control point will be relevant to each contaminant or group of contaminants.

The Framework analysis process begins with defining studies that may be needed to determine the effectiveness of controls associated with source water protection. Source water protection methods include identification of approaches that may be cost-effective and reliable in controlling a contaminant without the need for add-on treatment. The premise being that "no" treatment is the preferred approach to control any contaminant or group of contaminants in drinking water. This "no" treatment approach is the one that should yield the most public health benefit at the lowest overall cost. Control approaches that require add-on treatment will be less certain in assuring public health protection due to possibilities for human and mechanical failure, and will be more costly in the short and long-term. Source Management can be accomplished in a variety of ways for either surface or ground waters. These measures could include remediation of contaminated groundwater for a chemical contaminant or elimination of sources of microbial contaminants, such as, exclusion of livestock from waterways. Other potential interventions could include discontinued use of a contaminant of concern in the areas that contribute to the drinking water source and still others could be eliminated by mechanisms such as replacement with less toxic materials through "green chemistry" approaches.

Add-on treatment research includes exploration of novel treatment technologies, optimization of existing treatment processes and verification of performance for commercially ready technologies. Ideally, add-on treatment should control the contaminant in the simplest, low-cost manner without the generation of waste residuals or adverse effects to the distribution system. The starting place for this analysis begins with an evaluation of existing treatment trains to determine if they can control the contaminant in question to the level desired. If this analysis is not fruitful, additional treatment will need to be considered. New treatment processes should not interfere or reduce the effectiveness of existing treatment processes whose goals have been defined previously. Information on performance at various scales (bench, pilot and full-scale) must also be developed.

Add-on treatment technologies fall into a variety of categories including; physical-chemical removal (chemical and microbial contaminants), disinfection (microbial contaminants), and transformation processes (chemical contaminants).

Treatment processes involving physical-chemical removal do not destroy the contaminant. Examples of physical-chemical removal processes are coagulation, sedimentation and filtration, ion exchange, softening, membranes, and modified carbon adsorption. Disinfection treatment processes for microbiological contaminants include chlorination, chloramination, ozonation, ultra-violet irradiation and chlorine dioxide disinfection. Treatment technologies that transform chemical contaminants include processes such as biological treatment and electrochemical reduction. In the U.S., disinfection is the most common treatment used (U.S. EPA 1999).

The above listed treatment approaches are those that are most common and accepted by the industry. For any given contaminant requiring add-on treatment, it is prudent to explore new emerging technologies that may offer additional treatment alternatives. To assist the utility industry and states in accepting new innovative technologies, the Agency has created the Environmental Technology Verification Program (U.S. EPA 2000). This program is designed to verify the performance of commercially ready technologies to address important environmental problems facing the country. Verification protocols are developed through an open stakeholder driven process. The Drinking Water Systems Center has been very active in testing a number of classes of technologies including, *Cryptosporidium* filtration technologies, disinfection technologies and arsenic removal technologies. All verification reports and protocols are available at http://epa.gov.etv/.

Understanding the fate of the contaminant in the distribution system is another element of the research Framework. If it is demonstrated that there are distribution system effects for the contaminant in question, then control or management methods must be applied during distribution.

The fourth element of the Framework is to characterize any liquid or solid waste residuals generated as a result of the treatment process selected. Enough information must be available to determine how they should be managed and the long term environmental effects should they require disposal. Finally, cost must be assigned to each of the four major areas to begin to formulate acceptable strategies to achieve control goals.

ARSENIC IN DRINKING WATER: CASE STUDY

The recent lowering of the arsenic drinking water standard to 10 micrograms per liter serves as an excellent case study for application of the Framework. Priority research efforts conducted to support promulgation of the new standard were focused on optimization of existing treatment processes, add-on treatment technologies and residuals management issues (U.S. EPA 1998). The research plan scope did not include opportunities to control the contaminant through source water protection and did not address distribution system effects.

Studies to address possible source water protection approaches and distribution effects studies have been initiated recently. Approaches to control the contaminant at the source include examination of the feasibility of isolating zones in the subsurface where high arsenic waters are identified and well-pumping approaches to reduce the level of arsenic below the new standard.

Distribution system effects studies are also in progress. The release of arsenic-containing drinking water distribution system solids has been documented in one mid-sized Midwestern drinking water utility (Reiber 2000). The investigation revealed that the majority of arsenic (As) collected during an elevated arsenic episode was sorbed onto the particulate metal solids responsible for colored water complaints by consumers. This phenomenon has been confirmed by recent EPA studies where solids present in distribution systems were found to contain significant quantities of arsenic. The quantity of arsenic in the solids did not correlate with the arsenic concentration of the source or treated waters or the content of major elements in the solids. A concerning observation was that the solids that had been exposed to waters that contained only small levels of As (<10 µg/L) still concentrated relatively large amounts of arsenic (Lytle 2003). Because the Arsenic Rule requires arsenic to be monitored at the entry point into the distribution system (U.S. EPA 2001), elevated arsenic concentrations at the consumer's tap due to the release of arsenic from distribution system solids are possible. This new finding will be evaluated in the future when the rule is reexamined.

This case study demonstrates the value of considering the control of this drinking water contaminant in the context of the Framework.

EMERGING RESEARCH

One of the fundamental ways that is used to insure the safety of drinking water is to routinely sample and analyze for bacterial quality. The methods relied upon to conduct these evaluations are most often culture based techniques. However, important pathogenic organisms such as *Legionella pneumophila* are difficult to grow and enumerate from environmental samples. In recent years, DNA based analytical techniques have evolved and may provide more in-depth information on the types of organisms present in drinking water.

Recent studies using these new techniques have been conducted at the EPA's Test and Evaluation Facility in Cincinnati, Ohio (Meckes et al. 1999). The Facility is equipped with a Distribution System Simulator consisting of six independent ductile iron loops supplied with tap water from the Greater Cincinnati Water Works. The purpose of these studies was to better characterize the composition of microbial populations in the Simulator by direct sequence analysis of 16S rDNA clone libraries (Williams et al. 2003). This work has demonstrated the dominance of alpha-proteobacteria in the system water with two different disinfectant residuals. The shift from chlorine to monochloramine residual may have played a role in bacterial population dynamics.

Another area of emerging concern is drinking water security. This new area of study, fueled by worldwide concern over possible intentional contamination of drinking water, has highlighted a number of knowledge gaps. This potential threat to drinking water safety has even called into question the efficacy of some of the most fundamental drinking water protection practices. For example, boil water advisories are commonly issued when drinking water becomes contaminated during delivery or if treatment fails. The public is usually advised to bring the water to a boil to render it safe for consumption. Recent studies have been undertaken by EPA to determine the resistance of endospores of *Bacillus anthracis* and three strains of *Bacillus sphaericus* to the boiling process as it would normally be conducted by a water consumer (Rice 2003). Based upon the initial levels of endospores used in the study, the findings suggest that guidelines that call for bringing water to a rolling boil for 1 to 3 min in an open container would not be sufficient to inactivate endospores of *Bacillus anthracis*. Boiling water for five minutes in a covered vessel was sufficient to inactivate endospores of *Bacillus anthracis, Bacillus cereus,* and *Bacillus thuringiensis* by greater than four orders of magnitude. However, boiling in an uncovered vessel was not as effective.

Other research efforts related to water system security include the testing of monitoring and detection technologies that are needed to evaluate the safety of the drinking water on a more continuous and reliable basis. EPA studies have focused on evaluating the various instruments and developing performance criteria for on-line monitoring instrumentation (Haught 2003). Traditional parameters include temperature, dissolved oxygen, oxidation-reduction potential, free chlorine, pH and turbidity. The Agency has previously identified these parameters as reliably measured even through remote telemetry. New monitoring technologies are still focused on these more traditional parameters. While there are many new technologies being proposed to provide more real-time monitoring of a variety of chemicals and microbiological agents of concern in drinking water, it may be some time before they can be deployed and used to provide time relevant results to provide advance warning to drinking water suppliers.

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DEPOSITIONAL CHARACTERISTICS OF LAKE SEDIMENTS IN CANADA AS DETERMINED BY PB-210 AND Cs-137

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ABSTRACT

The geographical variation in atmospheric input fluxes of pollutants is of paramount importance for understanding the implications of atmospheric pollution. In regions with high levels of industrial and agricultural activity, the natural distribution of some pollutants could be affected by existing point sources of chemicals. Due to its geographic location and size, Canada offers opportunities for studying geographic variations in fluxes of airborne materials independently of local point sources. The sub-Arctic covers 53 percent of Canada and is very sparsely populated, hence most of Canada is not affected by point-source anthropogenic impacts. Most changes in loadings of contaminants reflect changes in regional atmospheric inputs. Some of the most convincing examples of this include synthetic organic compounds never used in the Arctic. To reconstruct histories of chemical contamination over the past 150 years, sedimentary records of 20 lakes have been examined. Fifty-four sediment cores collected from 1987 to 1993 were analyzed using Pb-210 ($t_{1/2}$=22.26 yr) and Cs-137 ($t_{1/2}$=30 yr) dating methods. A wide range of depositional characteristics including sedimentation rates, mixing depths, geochronologies of sedimentation, radionuclide inventories and fluxes were obtained. It was assumed that sediments from basins with no local industrial or domestic sources served as natural collecting systems recording the history of net inputs from the atmosphere. Since radionuclide inventories in the sediments are affected by physical, chemical and geological conditions, estimates of sediment focusing factors were made. Focusing factors were determined by dividing the measured excess Pb-210 flux in the core by the predicted atmospheric flux of excess Pb-210. The predicted flux values were determined experimentally from terrestrial soil profiles.

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1. INTRODUCTION

The geographical variation in atmospheric input fluxes of pollutants is of using mathematical models that consider these processes (Robbins fundamental importance for understanding the implications of atmospheric pollution. Due to its geographic location and size, Canada offers opportunities studying geographic variations in fluxes of airborne materials. The sub-Arctic covers 53 percent of Canada, hence most of Canada is not affected by point-source anthropogenic impacts; most changes in loadings of contaminants largely reflect changes in regional atmospheric inputs.

Lake sediments are natural repositories for contaminants and have often been used for studying the history of environmental contamination (Charles and Hites 1987, Oliver et al. 1989, Eisenreich et al. 1989, Krempler et al. 1992, Sanders et al. 1992). The burial of contaminants in sediments creates a stratigraphic record that reflects the chronology of their deposition. Input of contaminants has changed during the last 100-200 years due to industrialization. Pb-210 and Cs-137 (with half-lives of 22.26 and 30 years, respectively) have been used frequently to estimate history of deposition of sediment strata. However, apparent chronologies are affected by the post-depositional mobility (including biological mixing and diffusion) and sediment focusing. In cases where sediment mixing has occurred, sedimentation data can be interpreted 1978).

Focusing reflects accumulation of greater amounts of sediment in the deeper parts of lake basins (Davis et al. 1984). This brings with it additional radionuclides and contaminants from the watershed area due to erosion and seasonal flooding (Eakins et al. 1984). Sediment focusing depends on a variety of factors: lake geometry, climate conditions (amount of precipitation, wind and wave action), soil erosion within watershed, ratio of the watershed area to lake area, resuspension of previously deposited sediments, sedimentation rate, coring site location with respect to inflow and outflow streams, chemistry of the surrounded soils and sediments, etc. Focusing can confound the interpretation of changes in contaminant inputs. Knowledge of the focusing factors of lakes helps to distinguish local from regional events, and permits calculation of the areal-corrected net atmospheric fluxes of contaminants.

A main objective of this study was to estimate sediment focusing factors for Canadian sites. Since few soil profiles are available for Arctic locations, focusing factors we estimated from atmospheric radionuclide fallout based on northern hemisphere-wide measured data and measured input via soil profiles.

This study forms a part of a larger program that endeavors to reconstruct the history of contaminant inputs (heavy metals, organochlorines and polycyclic aromatic hydrocarbons) to Canadian lakes, as recorded in lake sediments.

2. MATERIALS AND METHODS

2.1. Site locations and physical characteristics of the lakes

Location of the lakes studied and their limnological characteristics are given in Table 1. Mean depth is determined as the ratio of the lake volume to its area. Drainage area excludes the lake area. The most southerly lakes in the study area are located on the Canadian Shield in Northwestern Ontario. Lakes 375 and 382 are in the Experimental Lakes Area (ELA) in boreal forest on Precambrian shield granites (Brunskill and Schindler 1971), generally with soft water (conductance = 20-100 $\mu S\ cm^{-1}$), often humic colored, and generally oligotrophic (Armstrong and Schindler 1971). Some geological and meteorological data for ELA presented in Table 1 are from Brunskill and Schindler (1971).

Lakes Green, Linge, Musclow, Orange, Sydney, and Trout are from the Red Lake District located just east of the Manitoba/Ontario border, 150 km north of ELA. The lakes situated there have an overall similarity to lakes in the ELA (Precambrian Shield geology, cold continental climate, and low conductance (Fee and Hecky 1992)). The lakes are only accessible by air, and like lakes in the ELA, there are no permanent residents in their drainage basin.

Lake Nipigon is the largest among the lakes investigated. It has geological and limnological characteristics that are similar to those of the Great Lakes (Fee and Hecky 1992).

Lakes Far and Hawk are situated at Saqvaqjuac, a Department of Fisheries and Oceans research site on the northwest coast of Hudson Bay. Information on geology, vegetation, climate and limnology of Saqvaqjuac is given in (Welch 1985). Saqvaqjuac is geologically similar to the ELA. Like the ELA, it has numerous small lakes. They are located on the Precambrian shield above the tree-line and appear to be ice-scour lakes of glacial origin. The water is generally oligotrophic and soft with low conductance (40-100 μS). Although Saqvaqjuac is at south of the Arctic Circle (66°N), it has a mid-arctic maritime climate (Welch 1985). The area is underlain by about 300 m of continuous permafrost with an average active layer of ~ 1 m in August. The lakes remain ice-covered for 9 months of the year.

Lakes Sophia and Amituk are located on Cornwallis Island in the Arctic zone on sedimentary limestone bedrock. Lake Sophia contains hypersaline waters (up to 2.5 times the salinity of seawater) in the monimolimnia (Page et al. 1984).

Lake Hazen, on Ellesmere Island, is the largest lake north of the Arctic Circle. It is situated on the Paleozoic sedimentary rocks of the Hazen Plateau (Deane 1958 and 1959). The lake basin was probably formed by a combination of geological faulting and glacial scour and, because of its elevation (158 m above sea level), was not inundated by marine waters following glaciation.

Arctic lakes present an interesting opportunity for applying radionuclide dating techniques. Much of the Arctic islands are covered with permanent ice and snow. Lakes Amituk and Sophia become ice-free for about 6 weeks annually. Lake Hazen receives runoff from glaciers located within its watershed during the brief Arctic summer and often remains ice-covered. Extensive ice cover would be expected to reduce the atmospheric inputs of radionuclides. On the other hand, periods of ice cover could be associated with still-water conditions and may create better opportunities for the settling of very fine particulates, which have strong adsorption ability with respect to contaminants.

Lakes Belot (Lac Belot) and Colville are situated in the Inuvik region on the Mackenzie lowland in the northwest part of the interior plains. Like the rest of the interior plains, the Mackenzie lowland is covered with clays and silts that accumulated on the floor of the huge glacial-age Lake Agassiz.

The lakes of the Yukon Territories are situated in the southern part of the Yukon Plateau, a basin-like area 600 to 900 m high. They all belong to the Yukon River drainage system. Due to its high elevation and latitudinal location, the southern Yukon has a frost-free period of about 45 days. Specific meteorological conditions of the southern Yukon are also determined by the barrier formed by the St. Elias and Coast ranges.

The investigated lakes ranged widely in size, from the smallest, Far Lake (surface area of 3.7 ha), to largest, Nipigon (484,800 ha). The lakes had more-or-less similar watershed area/lake area ratios, with exceptions of lakes Amituk, Sophia and, especially, Laberge. The lake depths ranged from shallow (Far Lake, maximum depth of 8.9 m) to very deep (Hazen Lake, 263 m). The lake basins had regular shapes with $Z:Z_{max}$ ranging from 0.24 to 0.45, with exceptions of lakes Fox (0.61) and Little Atlin (0.01).

2.2. Sediment collection, preparation and analysis

The sampling sites (Table 2) were determined from bathymetric and topographical maps of the lakes and surrounding area. The depositional zones were assumed, in most cases, to be the sites in the deepest parts of the lakes closest to lake inflows. Where possible, sampling was carried out in other parts of the deepest contour (FOX2, LAT2) and in different depth contours (L382 KB cores). Duplicate cores (e.g., LAB1 and LAB2) were also taken when possible.

The cores were sampled using 4 types of apparatus (Table 2), which were designed for different sediment types and to allow collection of varying amounts of sample per slice. Our original corer was a 5.1 cm diameter KB type gravity corer. Sediments sliced in 1 cm intervals yielded small (0.3-1.0 g) amounts of dried material per slice at the top where most of the Pb-210 datable history is contained. Although sufficient material was available for

Table 1. Locations and limnological characteristics of lakes investigated.

Location, lake	Latitude	Longitude	Mean depth, m (Z)	Maximal depth, m (Zmax)	Z:Zmax	Lake area, ha (Ao)	Drainage area, ha (Ad)	Ad:Ao	Volume, km^3
Northwestern Ontario									
375	49°45'N	93°47'W	11.6	30	0.39	18.7	210	11.2	
382	49°42'N	93°41'W	5.8	13	0.45	37.1	204.5	5.5	$2.15\cdot10^{-3}$
Green	51°N	94°W	7.7	19	0.40	89	234	2.6	$6.82\cdot10^{-3}$
Linge	51°15'N	94°18'W	8.4	23	0.36	706	2980	4.2	$5.91\cdot10^{-2}$
Musclo	51°24'N	94°57'W	19.2	46	0.42	2220	32850	14.8	0.427
Orange	51°N	94°W	14.4	29	0.50	167	1100	6.6	$2.40\cdot10^{-2}$
Sydney	50°41'N	94°25'W	20.0	73	0.27	5750	46400	8.1	1.15
Trout	51°15'N	93°15'W	13.6	49	0.28	34700	71800	2.1	4.72
Nipigon	49°50'N	88°31'W	58.5	143	0.41	484800	2450000	5.1	284
Yukon Territory									
Fox	61°14'N	135°28'W	28.6	47	0.61	1660	--	--	0.470
Kusawa	60°20'N	136°22'W	54.0	140	0.39	14222	--	--	7.72
Laberge	61°11'N	135°12'W	54.0	146	0.37	20100	2538500	126.3	10.8
Little Atlin	60°15'N	133°57'W	0.6	47	0.01	3790	--	--	$2.27\cdot10^{-2}$
Nunavut									
Far	63°42'N	90°40'W	3.6	8.9	0.40	3.7	16.6	4.5	$1.34\cdot10^{-4}$
Hawk	63°38'N	90°42'W	11.7	34.2	0.34	24.3	299.4	12.3	$2.83\cdot10^{-2}$
Amituk	75°03'N	93°48'W	10.0	42	0.24	58.8	2290	38.9	$5.88\cdot10^{-3}$
Sophia	75°07'N	93°35'W	20.0	55	0.36	330	6120	18.5	$6.60\cdot10^{-2}$
Hazen	81°45'N	71°30'W	85.0	263	0.32	53570	400000	7.5	45.5
Northwest Territories									
Belot	66°53'N	126°16'W	--	--	--	30250	--	--	--
Colville	67°10'N	126°00'W	--	--	--	45230	--	--	--

radiochemical work, little remained for other analyses. The 10 and 16 cm diameter KB corers were designed to take larger amounts of sediment per slice and allowed us to get better resolution by slicing the top 10 cm in 0.5 cm intervals. The 10 cm KB is very versatile and will work in most sediments but the 16 cm KB does not work at all in soft sediments and the only success with it has occurred in the Yukon lakes and in a sandy bay of Colville Lake (COL1). The boxcorer was designed for taking large slice amounts in both hard and soft sediments. It is about 80 inch length and resembles a tall Ekman dredge. It has a removable outer frame containing a stainless steel box (547 cm^2 in area) with pre cut slicing slots, which allows the core to be collected in 1.2 cm intervals. As the equipment used is heavy and sometimes bulky, an electric winch assembly was used to lower the corer into the sediments. In order to have a stable platform, all coring was done in the winter months through the ice. The corers were lowered slowly into the sediment with the aid of a recording sonar, which allowed 'viewing' the corer approaching the sediment by controlling the sonar window. The sediment profiles were sliced and bagged immediately after sampling and transferred back to the lab where they were freeze dried, ground and stored at 5^{o}C prior to analysis.

Radiochemical analyses were carried out using a number of analytical techniques. Five to ten grams of sediment were sealed in 60 x 15 mm plastic petri dishes, aged for 30 days and counted on a gamma spectrometer (Ge(Li) semi-conductor detector) for the determination of Cs-137 and Ra-226. In some cases, counting was done on a hyperpure germanium crystal and Pb-210 was determined directly along with Cs-137 and Ra-226 (Joshi 1987). One to three gram samples were analyzed for Pb-210 by leaching in 6N HCL in the presence of a Po-209 tracer, autoplating Po onto a silver disc (Flynn 1968) and counting the disc on an α-spectrometer to determine Pb-210 via its Po-210 daughter. Ra-226 was determined on selected slices by the radon de-emanation technique (Mathieu 1977, Wilkinson 1985). Excess Pb-210 was determined in each slice by subtracting the Ra-226 activity from the Pb-210 activity. Precise sample thickness was obtained by dividing the wet mass of sediment aliquot by its bulk density and area. Bulk densities, obtained from companion cores, were reasonably constant (1.12-1.17 g/cm^3) from 0 to 10 cm.

2.3. Methodology of estimating depositional characteristics of lake sediments

Using the lakes to study the mechanisms of environmental pollution requires the knowledge of the depositional characteristics, geochronologies of sedimentation and, especially, focusing factors for obtaining areal-corrected input fluxes of contaminants.

Net, dry mass sedimentation rates ω, g cm^{-2} yr^{-1} and geochronologies for each core were determined from four different models (Robbins 1978, Oldfield and Appleby 1984). All of them provide the least-square fit to log [excess Pb-210 activity] *vs*. total accumulation mass profile. The "simple" model (1) assumes a constant Pb-210 flux (Φ) and a constant dry-mass sedimentation rate. The sedimentation rates in this model are determined by a least-square fitting applied to the exponential part of the profile. In this model, T (i.e., the age of sediment stratum having a mass, m, g cm^{-2}) is given by

$$T = \frac{m}{\omega} \qquad \text{(Eq. 1)}$$

Model 2 (rapid steady-state mixing model, RSSM) reflects the effect of sediment mixing on the "simple" model. The RSSM assumes a constant Pb-210 flux and accumulation rate, and rapid steady state mixing throughout a surface zone of fixed thickness S beneath which no mixing occurred (Robbins 1978). In this case, the excess Pb-210 *vs*. mass - depth profile is expressed by the following equations (Eq. 2):

$$\begin{aligned} C_{Pb-210ex}(m) &= C_S && \text{at } m \le S \qquad \text{(Eq. 2)} \\ C_{Pb-210ex}(m) &= C_S e^{-\lambda_{Pb}(m-S)/\omega} && \text{at } m > S \end{aligned}$$

where $C_{Pb\text{-}210ex}(m)$ and C_S are the excesses of Pb-210 (Bq g^{-1}) in the core at mass-depth m and within the mixed zone, respectively; λ_{Pb} is the decay constant of Pb-210 (0.03114 yr^{-1}), S is the mixed depth in g cm^{-2}. The values of S and ω are determined from the weighted least-square fit of log [$C_{Pb\text{-}210ex}(m)$] *vs*. cumulative dry mass curve. The linear sedimentation rates in units of cm yr^{-1} were calculated by the RSSM as a mean value over the upper 10 cm. The slice ages are determined by Eq. 1.

When Pb-210 flux from the lake waters to the sediments remains constant but ω varies with time, the constant flux model 3 (CFM) is applicable for which the age of sediment stratum (T) is:

$$T = \frac{1}{\lambda_{Pb}} \ln\left[\sum A_{Pb-210ex} / \sum A_{Pb-210ex}(m)\right] \qquad \text{(Eq. 3)}$$

where $\sum A_{Pb-210ex}$ is the total integrated excess Pb-210 (inventory) in the sediment column in units of Bq cm^{-2} and $\sum A_{Pb-210ex}(m)$ is the integrated excess Pb-210 beneath sediments with cumulative dry mass m, and λ_{Pb} is the decay constant of Pb-210. The sedimentation rates are calculated from the formula

$$\omega = \frac{\lambda_{Pb} \sum A_{Pb-210ex}(m)}{C_{Pb-210ex}(m)} \qquad \text{(Eq. 4)}$$

When Pb-210 flux (Φ) and a dry mass sedimentation rate ω change proportionally to keep a constant specific Pb-210 activity, $C^{o}_{Pb-210ex} = \Phi / \omega$, model 4 (constant specific activity model, CAM) is applicable. CAM is feasible when, particularly, the main delivery pathway to the lake for atmospheric Pb-210 is the input from watersheds associated with the erosive input of fine surface particulates to which it is attached. According to this model, the age (*T*) corresponding to the sediment stratum at a mass-depth *m* is:

$$T = \frac{1}{\lambda_{Pb}} \ln[C^{o}_{Pb-210ex} / C_{Pb-210ex}(m)] \qquad \text{(Eq. 5)}$$

and the sedimentation rate is (Robbins 1978):

$$\omega = \frac{\lambda_{Pb} C_{Pb-210ex}(m)}{[dC_{Pb-210ex}(m) / dm]} \qquad \text{(Eq. 6)}$$

When the topmost Pb-210 activities are lower than those a few cm down in core, as is sometimes the case, model 4 yields negative sedimentation rates and times.

In this study, the sedimentation rates were also estimated, wherever possible, using Cs-137 as a discrete time marker (Robbins et al. 1978, Heit and Miller 1987). Cs-137 is a uniquely anthropogenic radionuclide originally introduced into the environment as a result of atomic weapons testing. Cs-137 is usually rapidly removed from the lake waters through particle scavenging and sedimentation (Robbins 1982), therefore; it might be expected that sedimentary profiles of Cs-137 would closely parallel the pattern of atmospheric deposition. The initial input of Cs-137 into the global environment is estimated to be 1952 ± 2 (Robbins et al. 1978, Ritchie and McHenry 1990) with measurable amounts in soils generally beginning in 1954 (Wise 1980, Longmore 1982), whereas significant atmospheric nuclear weapons testing was carried out until the signing of the Limited Test Ban Treaty which took effect in October 1963. Thus, well time-resolved sediment cores should demonstrate two distinguishable maxima - a major peak corresponding to 1963-1964 and a secondary peak occurring somewhere deeper in the sediment corresponding 1958-1959 (Ritchie and McHenry 1990). I The Cs-137 activity in sediments deposited after 1963 should decrease rapidly and there should be no downward tailing of Cs-137 below the depth corresponding to 1952 ± 2. The nature of deviations of the Cs-137 profiles from that relationship was discussed elsewhere (Davis R.B. et al.

1984, Robbins 1982, Robbins et al. 1990, Edgington et al. 1991). In this study, the median age of slice containing Cs-137 at a concentration above 5% of maximum Cs-137 activity in a core was taken as 1952 ± 2, whereas the median slice corresponding to the maximum activity of Cs-137 in a core was taken as the horizon representing the period of significant nuclear weapons testing, 1963 ± 1. Uncertainties in the position of the horizons were taken as the half-width of this interval. Sedimentation rates estimated from Cs-137 profile therefore correspond to the mean sedimentation rate over the three decades.

The inventories, I, Bq cm^{-2}, for radionuclides were calculated using Eq.7:

$$I = \sum_i m_i C_i \qquad \text{(Eq. 7)}$$

where m_i and C_i are the dry mass, g cm^{-2}, and radionuclide activity, Bq g^{-1}, measured for each sediment slice, respectively. The annual depositional Pb-210 fluxes (Bq cm^{-2} yr^{-1}) were all determined by multiplying total sediment inventory by the decay constant of Pb-210, λ_{Pb}. Fluxes calculated in this way are approximately 100-150 yr averaged and are independent of any model used for sedimentation rate estimation.

The intrinsic resolution time, $T^* = S/\omega$, is the time span over which a change in the input rate of a contaminant is not resolved in the sediment record (Eisenreich et al. 1989). However, as shown by Eisenreich et al. (1989), if contaminants are deposited with source function half-life shorter than those for Pb-210 and Cs-137, the contaminant profile may yield some information about geochronologies of contamination even in the mixed zone.

The focusing factors were calculated as the ratio of the depositional Pb-210 fluxes to the regional atmospheric Pb-210 fluxes or as ratio of total sediment radionuclide inventory to decay-corrected regional radionuclide inventory. Where possible, the Pb-210 atmospheric depositions were determined from soil profiles not influenced by erosion or focusing. In other cases, when snow or ice cover made the soil sampling impossible, the predicted values of atmospheric radionuclides deposition based on historical fallout were used.

3. RESULTS AND DISCUSSION

3.1 Depositional characteristics of lake sediments

Analysis of distribution of excess Pb-210 and Cs-137 activity in 54 cores showed that all of them fall into two categories. Representative "radionuclide activity vs. mass-depth" curves and age vs. mass-depth relationships are shown in Fig. 1. Plots for other cores are not shown for brevity. KB core KUS1 from Kusawa Lake exemplifies the cores, which are not disturbed by surficial mixing. For such cores, excess Pb-210 exponentially decreases upon increasing sediment depth, and Cs-137 activity shows distinct peak well corresponded to the period of most intensive atomic weapons testing. Box core 1 in Lake 382 represents cores affected by mixing. In this case, Pb-210 and Cs-137 profiles demonstrate a zone of constant activity in the surface sediments. In Lake 382, Cs-137 is present in slices deposited before 1952. Such a "rat tail-like" behavior also is due to mixing, diffusion or coring artifacts, which extends Cs-137 activity deeper into the core.

Depositional characteristics of the lakes studied obtained by analysis of radionuclide activity vs. mass-depth curves are summarized in Table 2. Mixing-corrected surface unsupported Pb-210 activities ranged from 0.04 to 2.94 Bq g^{-1}; herein Pb-210 surface activities generally tend to decrease with northern latitude. Pb-210 surface activities are functions of Pb-210 influx, mass sedimentation rate, and scavenging efficiency of the sediments, which depends on their physico-chemical properties.

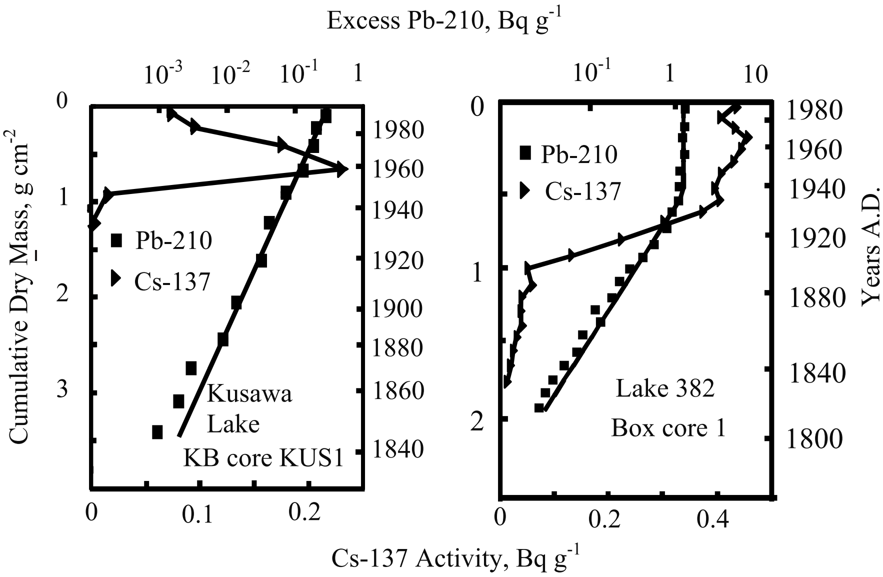

Figure 1. Excess Pb-210 and Cs-137 activity vs. mass-depth profiles and age-mass-depth relationships derived from Pb-210 data. For Pb-210 data, solid lines represent the best least-square fit to the data points obtained with RSSM model, which accounts for the surficial mixing of sediments.

Application of the RSSM model to the Pb-210 data yielded depths of the mixed zone (Table 2), *S*, defined as the solid mass per unit area (g cm^{-2}) or as a linear mixed depth (cm). Since the thickness of all slices in this study was compaction–corrected, both values are equivalent. In cores where *S* is very small (0 - 1 cm) it simply represents the water/sediment interface, and mixing should not be taken in consideration. Other cores demonstrate a sizable mixed zone, as for examples, cores from Lake 382 and Trout Lake, except core TL4. Mixing can be caused by the activity of benthic organisms (Robbins 1982), water currents or both. The extent of mixing is apparently related to the physical properties of the upper layer of the sediment. The depth of mixing tends to increase toward the centers of the depositional basins, where sediments are less consolidated (Robbins 1982). A plot of compaction-corrected mixed depths *vs*. mean sediment porosity in the upper 5 cm of the lakes studied (Fig. 2) shows that 90 % of the lakes are within an area limited by the mixed depth of 2 cm and porosity of 0.93. This means that substantial mixing does not usually occur in surface sediments with porosities < 0.93. Similar results were obtained for Great Lakes sediments (Robbins 1982).

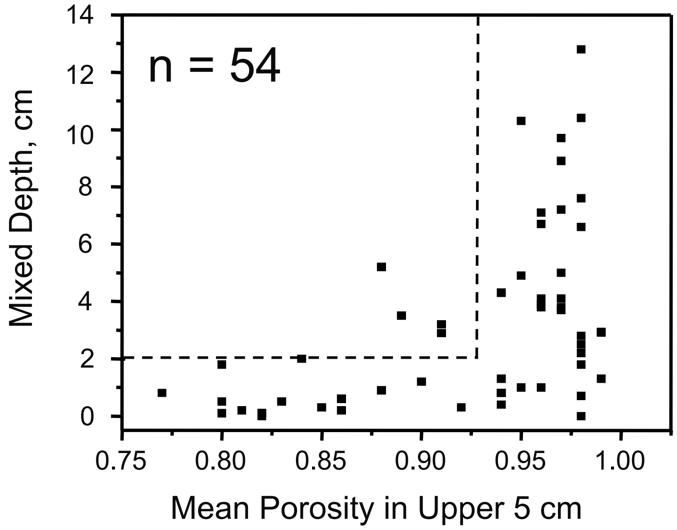

Figure 2. Relationship between compaction-corrected mixed depths and mean sediment porosities in upper 5 cm for lakes investigated.

Surficial mixing may play a significant role in the radionuclide settling processes at the water/sediment interface. For example, unsupported Pb-210 activities in the top slice, corrected for any surface mixing, are strongly correlated with mixed depths in sediments of Lake 382 ($r^2 = 0.83$, $n = 10$) and Trout Lake ($r^2 = 0.85$, $n = 6$) (Fig. 3), whereas, for the same two lakes, Pb-210 inventories were poorly or not at all correlated with mixed depth ($r^2 = 0.27$, $n = 10$ for Lake 382 and $r^2 = 0.02$, $n = 6$ for Trout Lake) (plots are not shown). These results are explicable in terms of the Pb-210 activity in upper slices reflecting equilibrium between the bottom water layer and the upper sediment layer and the exclusion of Pb-210 exchange between the particulate phase and pore water. Surface sediment mixing would tend to increase the excess Pb-210 in accordance with two mechanisms: (i) by increasing the scavenging efficiency of the surface sediments due to higher resuspension rates and increased contact time with ions in the bottom water layer, and (ii) by enrichment of the surface sediments with hydrous Fe–Mn oxides, which are highly efficient scavengers of ions (Megumi 1978, Aller et al. 1980), due to their post-depositional upward mobility (Carpenter et al. 1981).

Figure 4 shows that both mixed depth and intrinsic time resolutions tend to decrease with increasing northern latitude. Of 54 cores studied, 25 are situated above 60 ^{o}N, and only 4 of them had a mixed depth more than 2 cm reflecting low benthos activity and still-water conditions in high-latitudinal lakes. Only 3 cores from the lakes above the 60 ^{o}N parallel have T^* values greater than 12 years. Noteworthy, computed mixed depths in Sophia Lake range from 0.1 till 0.6 cm, but due to high sediment compaction (mean porosity in the upper 5 cm = 0.82-0.86), the intrinsic resolution times for this core was 5-12 years.

The average mass sedimentation rates and compaction-corrected linear sedimentation rates (cm yr^{-1}) for the last 100-150 years for all lakes are tabulated in Table 3. Linear sedimentation rates represent averages for the upper 10 cm of sediment. Usually, the mass sedimentation rates based on Pb-210 data were computed by the four methods. “Simple” model was not applied to lakes Amituk, Belot (cores BEL1 and BEL2), Colville, Green (core GL4), Nipigon (core 1) and Orange (core OL2) due to significant changes in Pb-210 profile slopes. The Pb-210 profiles in lakes Hazen and Sophia don’t show enough data points for an accurate linear regression. In general, the sedimentation rates calculated by various methods for the same lake were not statistically different. The mass sedimentation rates estimated by CFM and CAM models were less accurate than those calculated by “simple” and RSSM models.

In several cases, sediment geochronologies determined by Pb-210 data using Eqs. 1, 3, and 5 were verified by Cs-137 data. Data revealed considerable variation among the lakes studied. Surface activities ranged from 0.007 Bq g^{-1} dry wt in Lake Hazen to 0.78 Bq g^{-1} in Lake 375 (excluding Lac Belot, core BEL2, which had an uncharacteristically high 4 Bq g^{-1}). The Cs-137 profiles exhibit a subsurface maximum in lakes 375, Nipigon, Kusawa, Fox, Laberge, Little Atlin, Hawk, Lac Belot (core BEL1), and Hazen. Maximum activity occurs at 2-6 cm below the water/sediment interface. The occurrence of subsurface maximums suggests that some chronological information about recent contamination may be preserved in these sediments.

Maximum Cs-137 activity was observed at approximately the correct time (1961-1968) in lakes Nipigon (core 3 and 4), Kusawa (RSSM), Fox, Little Atlin, Lac Belot (core BEL1, CFM) and Hazen (RSSM). In other lakes, maximums of Cs-137 activity did not follow the pattern of atmospheric fallout

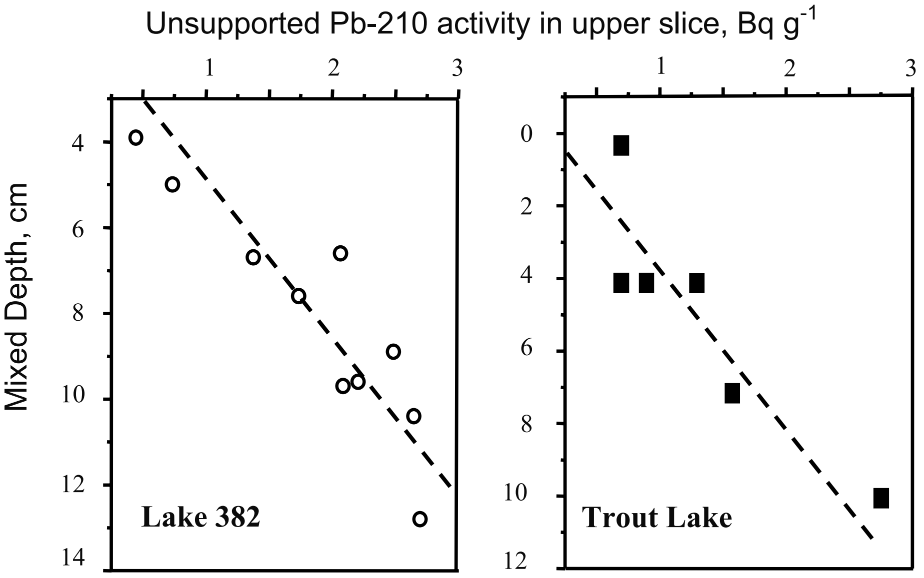

Figure 3. Relationships between mixing-corrected unsupported Pb-210 activities in upper slice and compaction-corrected mixed depth in Lake 382 and Trout Lake.

due to: (i) intensive surface mixing (Lakes 375 and Nipigon, core 1), (ii) post-depositional sediment redistribution in deep Lake Laberge, and (iii) Cs-137 mobility in soft Hawk Lake sediments. Sediment cores in lakes 382, Colville and Far show rather uniform Cs-137 activities in the upper slices that are in agreement with the computed mixed depths (Table 2). The Cs-137 profiles in lakes Amituk, Belot (cores BEL2 and BELBC), and Sophia did not exhibit subsurface maximum, although it would be expected from the Pb-210 data. The extent of penetration of Cs-137 in these sediments is shallow (depth of 2-3 cm). The absence of subsurface maximum in Lake Sophia may be caused by very low historical resolution in the cores.

Mass sedimentation rates calculated from Cs-137 data are presented in Table 3. The Cs-137 data do not yield meaningful values of ω in lakes 382, Nipigon, Laberge (KB cores LAB1 and LAB3), Colville, Amituk and Sophia due to the following reasons. Profiles in lakes 382, Nipigon and, probably, Colville, are dominated by mixing. Lake Laberge has a significant drainage area to lake area ratio and shows a large Cs-137 inventory/Pb-210 inventory

Table 2. Sedimentation, mixing, and inventory data for the lakes investigated.

Lake, core	Coring depth, m	Mean porosity in upper 5 cm	Supported Pb-210 activity, Bq/ g dry mass	Unsupported mixing-corrected Pb-210 activity in upper slice, Bq/g dry mass	Mixing depth		Intrinsic time resolution, yr	Radionuclide inventory Bq cm^{-2}		Ratio [Cs-137]/[Pb-210]	Pb-210 flux to sediment Bq m^{-2} yr^{-1}
					g cm^{-2}	cm		[Pb-210]	[Cs-137]		
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
375:											
Box core A	24	0.97	0.070	1.47	0.30	3.8	14	1.04	0.50	0.48	324
382:											
Box core 1	11	0.98	0.060	2.64	0.58	10.4	52	0.99	0.40	0.40	310
KB core A	11	0.98	0.035	1.73	0.42	7.6	25	0.94	--	--	290
KB core B	11	0.98	0.050	2.20	0.55	9.6	45	0.90	--	--	280
KB core C	10	0.98	0.040	2.69	0.80	12.8	107	0.73	--	--	230
KB core E	8	0.98	0.050	2.06	0.42	6.6	31	0.92	--	--	290
KB core G	6.5	0.97	0.045	2.48	0.76	8.9	100	0.70	--	--	218
KB core L	9	0.97	0.050	2.08	0.60	9.7	49	0.87	--	--	271
KB core O	3	0.96	0.015	0.44	0.46	3.9	11	0.60	--	--	187
KB core P	2.5	0.97	0.030	0.73	0.35	5.0	18	0.45	--	--	140
KB core Q	5	0.96	0.030	1.37	0.85	6.7	71	0.59	--	--	184
Green:											
KB core GL4	3	0.90	0.030	0.14	0.24	1.2	3	0.38	--	--	118
KB core GL5	18	0.99	0.032	2.94	0.08	2.9	9	0.92	--	--	286
KB core GL10	18	0.99	0.060	2.91	0.11	3.5	9	1.15	--	--	358

Table 2. Continued

1	2	3	4	5	6	7	8	9	10	11	12
Linge:											
KB core LL1	22	0.96	0.040	1.43	0.06	1.0	5	0.66	--	--	206
KB core LL2	22	0.97	0.040	1.86	0.26	3.7	12	1.29	--	--	402
Musclow:											
KB core ML1	42	0.96	0.030	1.38	0.88	7.1	20	2.03	--	--	632
Orange:											
KB core OL1	28	0.98	0.030	2.02	0.09	1.8	8	0.67	--	--	209
KB core OL2	21	0.96	0.040	1.95	0.41	3.8	42	0.66	--	--	205
Sydney:											
KB core SL1	64	0.95	0.040	1.46	0.70	4.9	26	1.29	--	--	400
Trout:											
KB core TL1	2	0.96	0.010	0.62	0.44	4.1	22	0.41	--	--	128
KB core TL3	49	0.97	0.030	0.89	0.38	4.1	4	2.92	--	--	910
KB core TL4	29	0.83	0.030	0.61	0.04	0.5	2	0.46	--	--	143
KB core TL5	23	0.95	0.030	2.76	1.61	10.3	144	1.07	--	--	333
KB core TL10	42	0.94	0.030	1.24	0.77	4.3	35	0.91	--	--	283
KB core TL12	30	0.97	0.030	1.61	0.75	7.2	31	1.30	--	--	405
Nipigon:											
KB core 1	142	0.88	0.027	1.05	1.87	5.2	46	1.50	1.18	0.79	467
KB core 3	92	0.84	0.027	0.53	0.98	2.0	12	1.46	0.78	0.53	455
KB core 4	142	0.89	0.027	0.69	0.99	3.5	17	1.37	0.80	0.58	427
Fox:											
KB core FOX1	47	0.94	0.014	0.45	0.15	1.3	12	0.19	0.11	0.58	60
KB core FOX2	43.5	0.95	0.014	0.52	0.09	1.0	11	0.15	0.09	0.60	47

Table 2. Continued

1	2	3	4	5	6	7	8	9	10	11	12
Kusawa:											
KB core KUS1	49	0.88	0.075	0.28	0.09	0.9	4	0.21	0.11	0.52	65
Laberge:											
KB core LAB1	140	0.77	0.050	0.10	0.27	0.8	4	0.25	0.25	1.00	78
KB core LAB2	140	0.80	0.055	0.10	0.04	0.1	1	0.22	--	--	68
KB core LAB3	138	0.81	0.052	0.13	0.05	0.2	1	0.27	0.20	0.74	84
KB core LAB4	138	0.82	0.052	0.11	0.03	0.1	0	0.25	--	--	78
Little Atlin:											
KB core LAT1	41	0.91	0.065	0.16	0.72	3.2	10	0.38	--	--	118
KB core LAT2	36	0.91	0.065	0.17	0.69	2.9	16	0.24	0.16	0.67	75
Far:											
Box core A	8.9	0.98	0.020	1.70	0.17	2.8	20	0.45	0.16	0.36	140
Box core B	8.9	0.98	0.029	1.24	0.04	0.7	5	0.38	--	--	118
Hawk:											
Box core A	34	0.99	0.008	2.22	0.02	1.3	3	0.41	0.07	0.17	128
Box core B	34	0.98	0.008	1.81	0.00	0.0	0	0.53	--	--	165
Amituk:											
KB core A	41	0.82	0.030	0.45	0.01	0.0	0	0.58	0.17	0.29	180
KB core B	41	0.80	0.030	0.45	0.14	0.5	3	0.57	--	--	177
Sophia:											
Box core A	52	0.86	0.030	0.81	0.06	0.2	5	0.29	0.04	0.14	90
Box core B	52	0.86	0.030	0.65	0.15	0.6	12	0.28	0.04	0.14	87
KB core A	52	0.85	0.028	0.77	0.06	0.3	8	0.26	--	--	80
KB core B	52	0.82	0.020	0.55	0.04	0.1	7	0.23	--	--	70

Table 2. Continued.

1	2	3	4	5	6	7	8	9	10	11	12
Hazen:											
Box core A	254	0.80	0.04	0.04	0.50	1.8	18	0.05	0.06	1.2	14
Belot:											
KB core BEL1	56	0.94	0.037	1.00	0.05	0.8	5	0.35	0.14	0.40	109
KB core BEL2	52	0.92	0.037	0.52	0.03	0.3	3	0.18	0.30	1.70	60
Box core BELBC	57	0.94	0.045	0.47	0.11	0.8	6	0.33	0.10	0.30	103
Colville:											
KB core COL1	15.5	0.94	0.036	0.26	0.02	0.4	1	0.16	--	--	50
KB core COL2	14.5	0.98	0.036	0.46	0.13	2.5	9	0.22	0.12	0.55	69

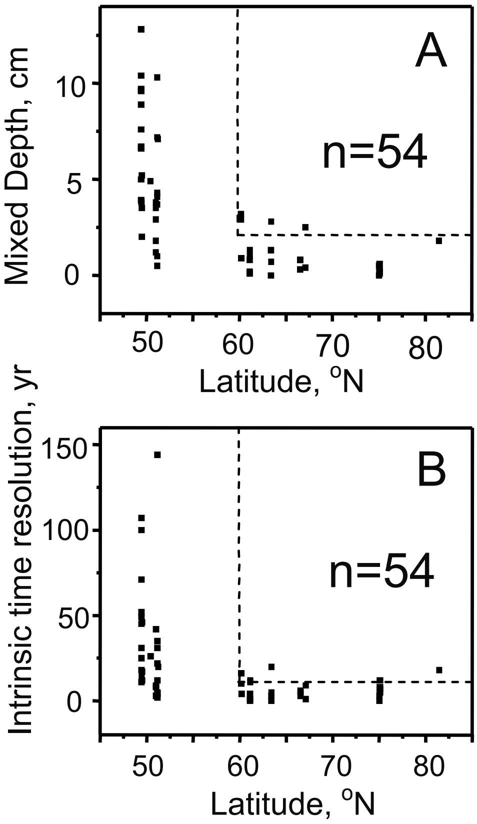

Figure 4. Latitudinal distribution of the compaction-corrected mixed depth (A) and intrinsic time resolution (B) in the lakes studied. Dashed lines correspond to 60°N and mixed depth of 2 cm (A) or to intrinsic time resolution of 12 yr (B).

ratio. In stratigraphically normal cores, the latter ranges from 0.4 to 0.6 (Robbins et al. 1990). The abnormalities point at substantial influence of the catchment area on the Cs-137 input flux and chronology. In lakes 375 and Hawk, the sedimentation rates calculated from Cs-137 appearance in cores agreed well with those estimated with Pb-210. In contrast, the sedimentation rates calculated from the maximum of Cs-137 activity were 3-4 times smaller, probably, due to post-depositional mobility of Cs-137 in soft lake sediments (Davis R.B. et al 1984). The reasons for the distinction of ω calculated with Pb-210 and Cs-137 data in cores from lakes Amituk and Sophia will be discussed below. Noteworthy, the values of sedimentation rates based on Cs-137 appearance in cores is generally larger than those calculated from the maximum of Cs-137 activity due to mixing, which extends Cs-137 deeper into the core with respect to the 1952 ± 2 horizon estimated from the Pb-210 geochronology.

3.2. Estimation of focusing factors of the lakes investigated

3.2.1. *Sources and transport of atmospheric Pb-210 in Canada*

Atmospheric Pb-210 flux directly depends on the amount of Rn-222 (half-life 3.8 days) emanated from the land surface (Jaworowski 1966, Kirichenko 1970). Emanation of Rn-222 is affected by the mechanical structure of the land surface layer, diffusion processes in the ground and the dynamic state of the atmosphere. A lower release of Rn-222 into the atmosphere can be expected in regions covered by forests. Lands covered by permafrost or glaciers are unlikely to exhale the Rn-222 in substantial amounts. Geographical distribution of atmospheric flux of Pb-210 is characterized by a maximum at 30-40^{o} N latitude, a minimum in the equatorial zone, and larger quantities in the northern hemisphere than in southern hemisphere (Rangarajan et al. 1976). This distribution is well correlated with global distribution of the land surface area (Sverdrup et al. 1949). Fractions of the total North American land area (excluding permafrost area and glaciers) obtained by digital mapping methods and Pb-210 atmospheric fluxes experimentally estimated from the soil profiles and artificial collecting systems (this study, Shell 1977, Nozaki et al. 1978, Fisenne et al. 1980) *vs*. northern latitude are plotted in Fig. 5. It shows that the distribution of atmospheric Pb-210 generally follows the fraction of total land area. This relationship does not hold for Hazen Lake, for which no deposition at all would be expected, and Seattle, Washington, showing rather lower atmospheric Pb-210 flux. Seattle is generally upwind of the North American continent and it is reasonable that the Pb-210 atmospheric flux would be lower here than locations downwind of North America. These deviations manifest the existence of certain atmospheric long-range transport phenomena, which cause the redistribution of atmospheric Pb-210 across North America. The mean residence time of Pb-210 in the atmosphere is 5-10 days (Krishnaswami and Lal 1978), which means that its delivery to the high north latitudes occurs within relatively short periods of time.

Table 3. Calculated sedimentation rates in the lakes investigated

Lake, core	Compaction-corrected linear sed. rate based on Pb-210 data, cm yr^{-1}	Mass sedimentation rate based on Pb-210 data, g m^{-2} yr^{-1}				Mass sedimentation rate based on Cs-137 data, g m^{-2} yr^{-1}	
		Simple model (1)	RSSM (2)	CFM (3)	CAM (4)	By maximal activity	By appearance in core
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
375:							
Box core A	0.22	112 ± 9	210 ± 6	151 ± 106	--	51 ± 3	182 ± 9
382:							
Box core 1	0.20	111 ± 4	111 ± 2	135 ± 57	--	--	436 ± 23
KB core A	0.28	176 ± 4	167 ± 7	159 ± 50	--	--	--
KB core B	0.21	141 ± 8	122 ± 7	159 ± 63	--	--	--
KB core C	0.13	89 ± 10	75 ± 6	144 ± 77	--	--	--
KB core E	0.20	160 ± 23	134 ± 4	143 ± 64	--	--	--
KB core G	0.09	73 ± 12	76 ± 4	153 ± 93	--	--	--
KB core L	0.20	138 ± 9	123 ± 4	157 ± 78	--	--	--
KB core O	0.24	371 ± 242	421 ± 10	315 ± 97	--	--	--
KB core P	0.20	185 ± 38	189 ± 8	162 ± 64	--	--	--
KB core Q	0.09	108 ± 10	120 ± 4	195 ± 95	--	--	--
Green:							
KB core GL4	0.19	--	796 ± 78	616 ± 160	--	--	--
KB core GL5	0.21	101 ± 2	96 ± 2	85 ± 21	--	--	--
KB core GL10	0.28	129 ± 3	121 ± 2	133 ± 118	--	--	--
Linge:							
KB core LL1	0.11	158 ± 4	132 ± 3	123 ± 48	132 ± 41	--	--
KB core LL2	0.12	192 ± 7	210 ± 4	231 ± 154	215 ± 171	--	--

Table 3 continued

Musclow:							
KB core ML1	0.31	468 ± 7	450 ± 5	457 ± 102	--	--	--
Orange:							
KB core OL1	0.11	110 ± 2	102 ± 2	87 ± 25	173 ± 200	--	--
KB core OL2	0.08	--	99 ± 3	125 ± 60	--	--	--

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Sydney:							
KB core SL1	0.14	269 ± 6	268 ± 5	300 ± 100	300 ± 100	--	--
Trout:							
KB core TL1	0.15	259 ± 13	202 ± 5	248 ± 109	--	--	--
KB core TL3	0.71	937 ± 84	975 ± 154	1018 ± 57	--	--	--
KB core TL4	0.04	260 ± 29	219 ± 8	213 ± 14	239 ± 70	--	--
KB core TL5	0.07	150 ± 10	112 ± 5	285 ± 185	--	--	--
KB core TL10	0.10	213 ± 9	220 ± 6	247 ± 74	315 ± 200	--	--
KB core TL12	0.21	264 ± 7	244 ± 5	265 ± 106	--	--	--
Nipigon:							
KB core 1	0.10	--	411 ± 6	497 ± 164	--	730 ± 26	900 ± 42
KB core 3	0.17	920 ± 20	835 ± 11	756 ± 129	--	--	--
KB core 4	0.17	551 ± 17	599 ± 8	574 ± 167	--	--	--
Fox:							
KB core FOX1	0.06	119 ± 4	126 ± 2	114 ± 34	--	103 ± 3	224 ± 8
KB core FOX2	0.05	81 ± 2	81 ± 1	73 ± 32	78 ± 19	76 ± 3	164 ± 8
Kusawa:							
KB core KUS1	0.13	227 ± 11	218 ± 15	278 ± 192	212 ± 57	233 ± 8	230 ± 11
Laberge:							
KB core LAB1	0.10	591 ± 48	732 ± 37	814 ± 973	--	1371 ± 47	1303 ± 62
KB core LAB1	0.10	656 ± 26	669 ± 25	583 ± 414	--	--	--
KB core LAB1	0.09	650 ± 31	611 ± 17	480 ± 108	627 ± 215	849 ± 29	1026 ± 48
KB core LAB1	0.09	561 ± 24	595 ± 20	414 ± 108	--	--	--

Table 3. Continued

Little Atlin:							
KB core LAT1	0.26	813 ± 36	703 ± 29	695 ± 247	--	--	--
KB core LAT2	0.14	390 ± 22	421 ± 21	405 ± 91	--	473 ± 16	503 ± 23
Far:							
Box core A	0.10	77 ± 11	70 ± 2	88 ± 34	138 ± 120	79 ± 3	251 ± 13
Box core B	0.11	74 ± 26	81 ± 2	74 ± 2	83 ± 31	--	--
Hawk:							
Box core A	0.11	51 ± 4	56 ± 1	37 ± 8	95 ± 36	16 ± 1	42 ± 2
Box core B	0.16	65 ± 5	90 ± 1	68 ± 14	92 ± 36	--	--
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Amituk:							
KB core A	0.06	--	367 ± 9	220 ± 100	320 ± 200	--	113 ± 5
KB core B	0.07	--	519 ± 15	350 ± 80	410 ± 200	--	--
Sophia:							
Box core A	0.02	--	114 ± 4	90 ± 30	120 ± 50	--	65 ± 3
Box core B	0.01	--	121 ± 5	70 ± 10	80 ± 1	--	143 ± 7
KB core A	0.03	--	75 ± 3	70 ± 40	130 ± 50	--	--
KB core A	0.03	--	62 ± 1	30 ± 20	130 ± 20	--	--
Hazen:							
Box core A	0.06	--	278 ± 24	167 ± 98	--	278 ± 11	1189 ± 60
Belot:							
KB core BEL1	0.06	--	104 ± 2	102 ± 36	155 ± 33	--	113 ± 5
KB core BEL1	0.04	--	97 ± 1	106 ± 47	--	--	--
Box core BEL	0.10	184 ± 11	188 ± 4	165 ± 59	232 ± 162	--	--
Colville:							
KB core COL1	0.06	--	183 ± 4	220 ± 202	--	--	--
KB core COL1	0.17	--	140 ± 3	154 ± 114	172 ± 110	--	305 ± 14

that the distribution of atmospheric Pb-210 generally follows the fraction of total land area. This relationship does not hold for Hazen Lake, for which no deposition at all would be expected, and Seattle, Washington, showing rather lower atmospheric Pb-210 flux. Seattle is generally upwind of the North American continent and it is reasonable that the Pb-210 atmospheric flux would be lower here than locations downwind of North America. These deviations manifest the existence of certain atmospheric long-range transport phenomena, which cause the redistribution of atmospheric Pb-210 across North America. The mean residence time of Pb-210 in the atmosphere is 5-10 days (Krishnaswami and Lal 1978), which means that its delivery to the high north latitudes occurs within relatively short periods of time.

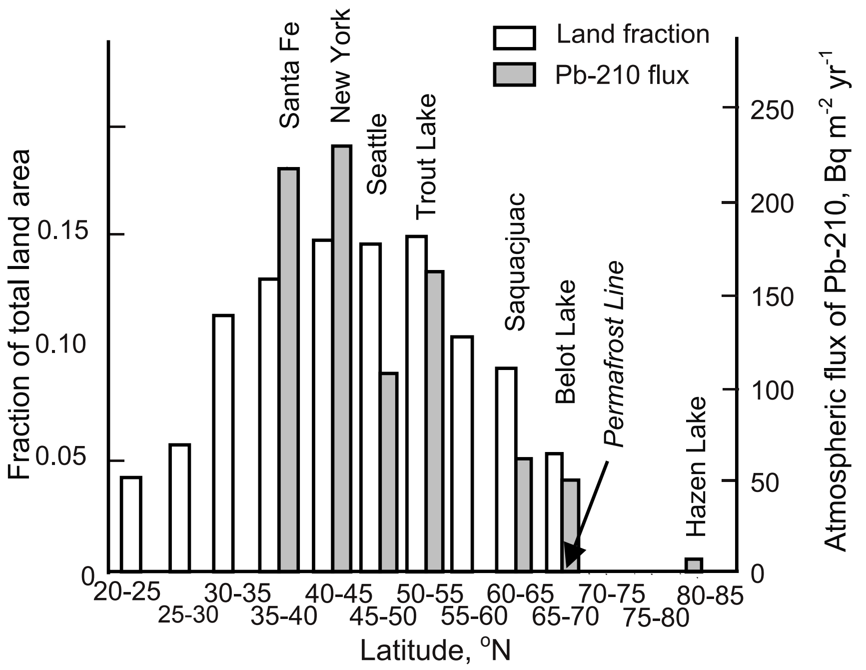

Figure 5. Fraction of total North America land area (excluding permafrost area and glaciers) and Pb-210 atmospheric flux vs. northern latitude.

The transport of terrestrial Pb-210 over the North Pacific Ocean was modeled by Nozaki and Tsunogai (1973). Since the regions of Canada covered by water, permafrost and glaciers are not considered as emanating Rn-222, they could be regarded as the "ocean" with a coastline that coincides with the permafrost border. Assuming the existence of atmospheric delivery process directed from the vast continent to the "ocean" and that Pb-210 is transported one-dimensionally along the direction x with constant parcel velocity, the horizontal distribution of Pb-210 in the atmosphere can be expressed using the equation:

$$\frac{dI_a}{dt} = -K_x \frac{dC_a}{dx} + P - (\lambda_{Pb} + \lambda_a) I_a \qquad \text{(Eq. 8)}$$

where I_a is the total amount of Pb-210 in the vertical air column, Bq m^{-2}, C_a is the concentration of Pb-210 in the air column, Bq m^{-3}, P is a production rate of Pb-210 from Rn-222 in the atmosphere, Bq m^{-2}s^{-1}; λ_{Pb} is the decay constant of Pb-210 (~10^{-9} s^{-1}), λ_a is the mean removal rate of Pb-210 from the atmosphere determined as the reciprocal of the mean residence time in the atmosphere, T_r. Assuming T_r = 7.5 days (Krishnaswami and Lal 1978) the λ_a is 1.5·10^{-6} s^{-1}. Here the parcel velocity is expressed in the form of the horizontal eddy diffusion coefficient, K_x, m^2 s^{-1}. Production rate P could be expressed as

$$P = \Phi_o \exp[(-\lambda_{Rn} / K_x)^{1/2} x]$$

where Φ_O is a production rate of Pb-210 at x = 0 and λ_{Rn} is the decay constant of Rn-222 (2.1·10^{-6} s^{-1}).

Assuming $I_a = C_a \cdot H$, where H is a height of atmospheric column, $\lambda_{Pb} << \lambda_a$ and $dI_a/dx = 0$ (steady state conditions), the solution of Eq. 8 is

$$C_a(x) = C_a(0)\exp(-\frac{\lambda_a H}{K_x}x) - \frac{\Phi_o}{\lambda_a H - (\lambda_{Rn} K_x)^{1/2}} \left\{ \exp(-\frac{\lambda_a H}{K_x}x) - \exp[-(\frac{\lambda_{Rn}}{K_x})^{1/2} x] \right\}$$

where C_a (0) is the concentration of Pb-210 in the air column at permafrost border (x = 0). Continuous permafrost within 60°–100° W longitudinal band begins approximately at 60° N (Permafrost 1978). The concentration of Pb-210 in surface air, 0.3 Bq/ 1000 m^3, estimated from observations over Lake Baikal, Russia (50°–55° N) (Edgington et al. 1991) can be taken as $C_a(0)$.

Production rate (Φ_O), 1.7·10^{-6} Bq m^{-2} s^{-1}, estimated for the north of Russia, near the ocean, containing forests with marshes, podsol, and turf soils, can be adopted for calculations (Kirichenko 1970). Rn-222, which emanates from the land areas, is mixed rapidly upward into the upper troposphere-low stratosphere and there decays to Pb-210 (Peirson et al. 1966, Shell 1977). Thus, the height of low stratosphere (14.3 km) (Peirson et al. 1966) can be used as the value of H.

Simulated distribution of Pb-210 concentration in the air column over permafrost and glacieral areas of Canada in the 60° – 100° W longitudinal band as function of latitude and mean parcel velocity is shown in Fig. 6. Since there are no reported measurements of Pb-210 air concentration in the Canadian Arctic, the concentration of Pb-210 in surface air observed in Thule, Greenland (76.5° N) (Patterson and Lockhart 1964) was adopted to the viability of the simulation. It can be seen that the parcel velocity ranging from $3{\cdot}10^5$ m^2 s^{-1} to $3{\cdot}10^6$ m^2 s^{-1} fits the observed data well. The above values are in good agreement with the mean annual atmospheric values of the meridianal eddy diffusion coefficient for interzonal atmospheric exchange from the northern boreal to northern polar zone, $(3.3 \pm 1.4){\cdot}10^6$ m^2 s^{-1}, estimated by Peixoto and Oort (1992). It clearly supports the notion that Pb-210 produced in the temperate zone through the emanation of Rn-222 could be transported as far as the Canadian Arctic by atmospheric processes, which include interzonal exchange and Pb-210 deposition via wet precipitation and dry fallout.

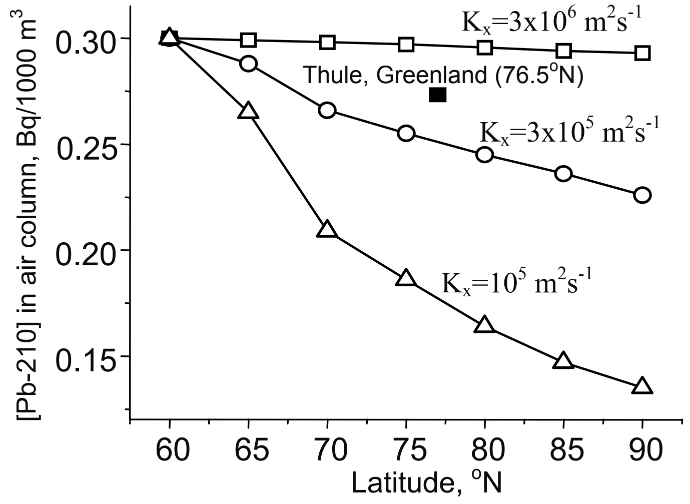

Figure 6. Predicted latitudinal distribution of Pb-210 concentration in surface air in Canada.

3.2.2. *Calculation of areal atmospheric Pb-210 fluxes and decay corrected Cs-137 inventories over the lakes investigated*

In this study, atmospheric Pb-210 fluxes were experimentally determined from undisturbed soil profiles in the vicinity of lakes: 375, Trout, Belot, Hazen, Far, and Hawk. The lack of these measurements for other locations necessitates the theoretical prediction of atmospheric Pb-210 fallout over the lakes studied. It was conducted by two different methods and the results are presented in Table 5.

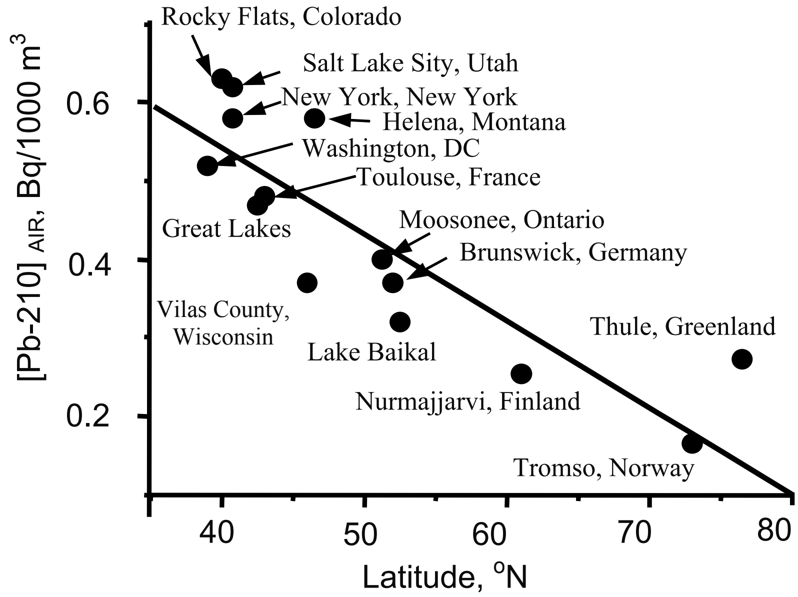

Figure 7. Latitudinal distribution of the Pb-210 concentration in surface air in the northern hemisphere above 38°N parallel.

The first method is based on the calculation of atmospheric Pb-210 fluxes, Φ_{atm}, from Pb-210 concentration in surface air, C_{atm} (Bq/1000 m^3), and total precipitation, p (rainfall and snowfall, cm month^{-1}), over the study lakes by empirical equation (Pelletier et al. 1964):

$$\Phi_{atm} = KC_{atm}\left[1 - \exp(-0.04p)\right] \qquad \text{(Eq. 10)}$$

where K is an empirical constant. Concentrations of Pb-210 in the surface air were estimated on the basis of regression analysis of data available for some locations in the northern hemisphere. They are plotted against latitude in Fig. 7. Data were collected from Patterson and Lockhart (1964), EML-395 (1981), Edgington et al. (1991), Talbot and Andren (1983). Regression analysis gives the following equation:

$$C_{atm} = 0.92 - 0.01N\,, \quad r^2 = 0.6, n = 9 \qquad \text{(Eq. 11)}$$

where N is a value of northern latitude.

Values of the total atmospheric precipitation, rainfall and snowfall, were determined on the basis of regression analysis of the long-term data observed across Canada in 1951-1980 (Precipitation 1982). Measured and calculated data are plotted against latitude in Fig. 8. Regression analysis was conducted for the four different longitudinal bands: (1) along the Canadian

Atlantic coast, 72° ± 10° W, (2) along mid-continental transect, 93° ± 10° W, (3) over the Mackenzie lowland of Northwest Territories, 127° ± 4° W, and (4) over the Yukon Territory, 135° ± 4° W.

The following regression equations were obtained:

(1) From 45° N till 60° N: $p = 24.6 - 0.35\ N$, $r^2 = 0.86$, $n = 9$, and from 60° N till 82° N: $p = 8.1 - 0.09\ N$, $r^2 = 0.75$, $n = 10$.

(2) From 48° till 60° N: $p = 16.8 - 0.23\ N$, $r^2 = 0.66$, $n = 12$, and from 60° N till 80° N: $p = 8.9 - 0.11\ N$, $r^2 = 0.92$, $n = 9$.

Within each of the above longitudinal bands, the latitudinal dependence of precipitation is described by two linear relationships. It corresponds to the climatic conditions in these regions, as the 60 °N parallel can be considered as a border of continuous permafrost zone.
(3) Above 55 °N parallel: $p = 15.6 - 0.20\ N$, $r^2 = 0.84$, $n = 11$.
(4) Above 60 °N parallel: $p = 5.7 - 0.06\ N$, $r^2 = 0.19$, $n = 12$.

In the last case, the correlation is weak but the amounts of precipitation do not vary too much throughout this zone, namely from 2 to 3 cm month^{-1}, and the error of estimation should not be too large.

The value of K was calculated to be 0.2 using data observed for Saqvaqjuac region, $\Phi_{atm} = 0.006$ Bq cm^{-2} yr-1 (this study), $p = 2.4$ cm month^{1} (Welch 1985) and $C_{atm} = 0.33$ Bq per 1000 m^3 (calculated by Eq. 1). Values of atmospheric Pb-210 fluxes calculated by Eq. 10 are presented in Table 5.

The second method is based on regression analysis of the northern hemisphere-wide atmospheric Pb-210 flux data experimentally estimated using natural and artificial collecting systems. The natural collecting systems included soil, salt marsh and glacier profiles. The data are presented in Table 4. It can be seen that the maximum atmospheric Pb-210 flux takes place in the temperate zone at 38°-40 °N. Two kinds of regression analysis were applied to the data listed in Table 4 above 40 °N parallel. Exponential regression analysis yields the following empirical equation:

Linear analysis yields two regression equations for the different latitudinal bands:
from 40 °N - 60 °N

$$\Phi_{atm} = 752 - 11.7\ N,\ r^2 = 0.52,\ n = 12 \qquad \text{(Eq. 12)}$$

$$\Phi_{atm} = 10069 \exp(-0.083\ N),\ \text{Bq m}^{-2}\ \text{yr}^{-1},\ r^2 = 0.94,\ n = 17 \qquad \text{(Eq. 13)}$$

and from 60 °N - 82 °N

$$\Phi_{atm} = 253 - 3.0\,N,\ r^2 = 0.99,\ n = 5 \qquad \text{(Eq. 14)}$$

Using Eq. 13, one can calculate an atmospheric Pb-210 flux over the Great Lakes (40°-50°N) ranging from 223-282 Bq m^{-2} yr^{-1}, which corresponds well

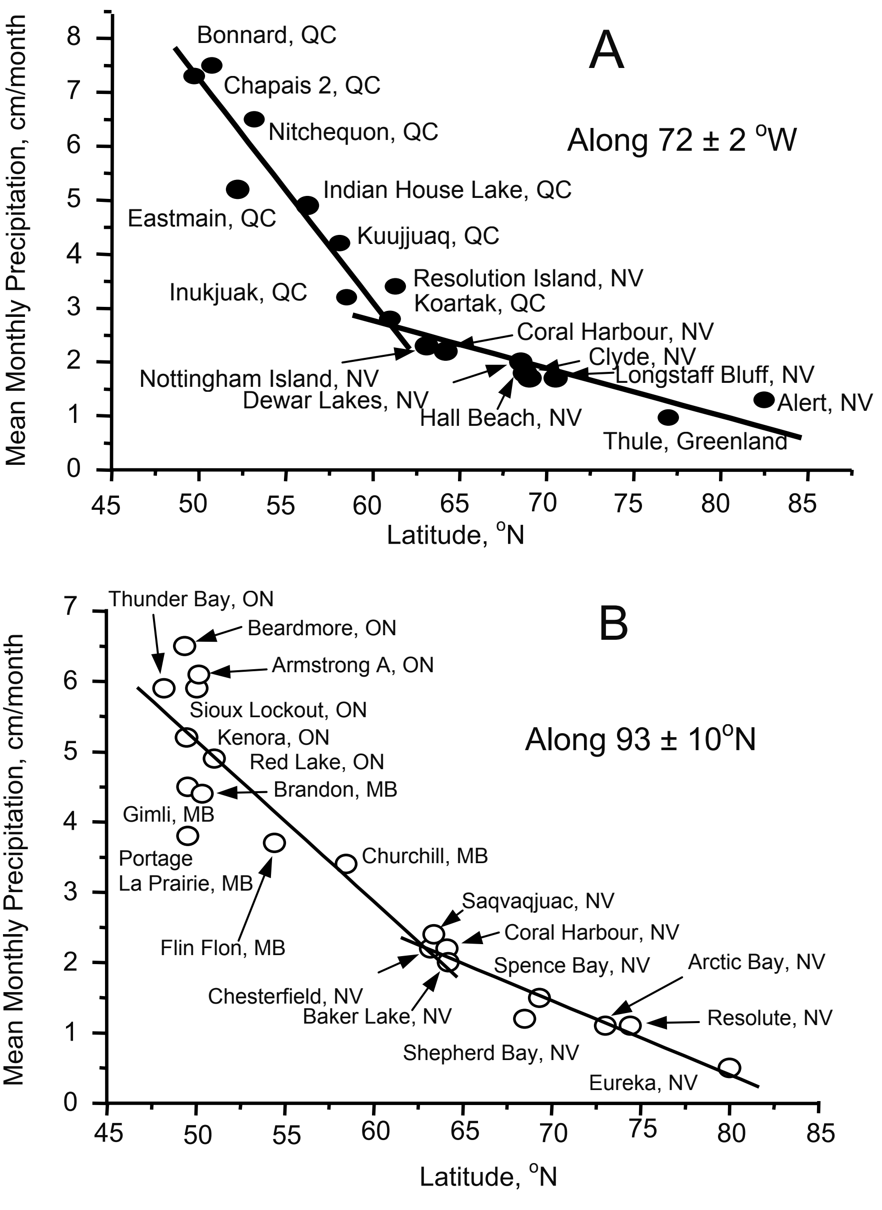

Figure 8 A and B. Monthly averaged total atmospheric precipitation (rainfall and snowfall) vs. northern latitude in Canada.

to experimentally estimated flux for this area (Edgington et al. 1991).

Atmospheric Pb-210 fluxes calculated by Eq. 12, 13 and 14 are presented in Table 5. Both exponential and linear regression analysis yield similar results with exceptions of the Inuvik region and Hazen Lake.

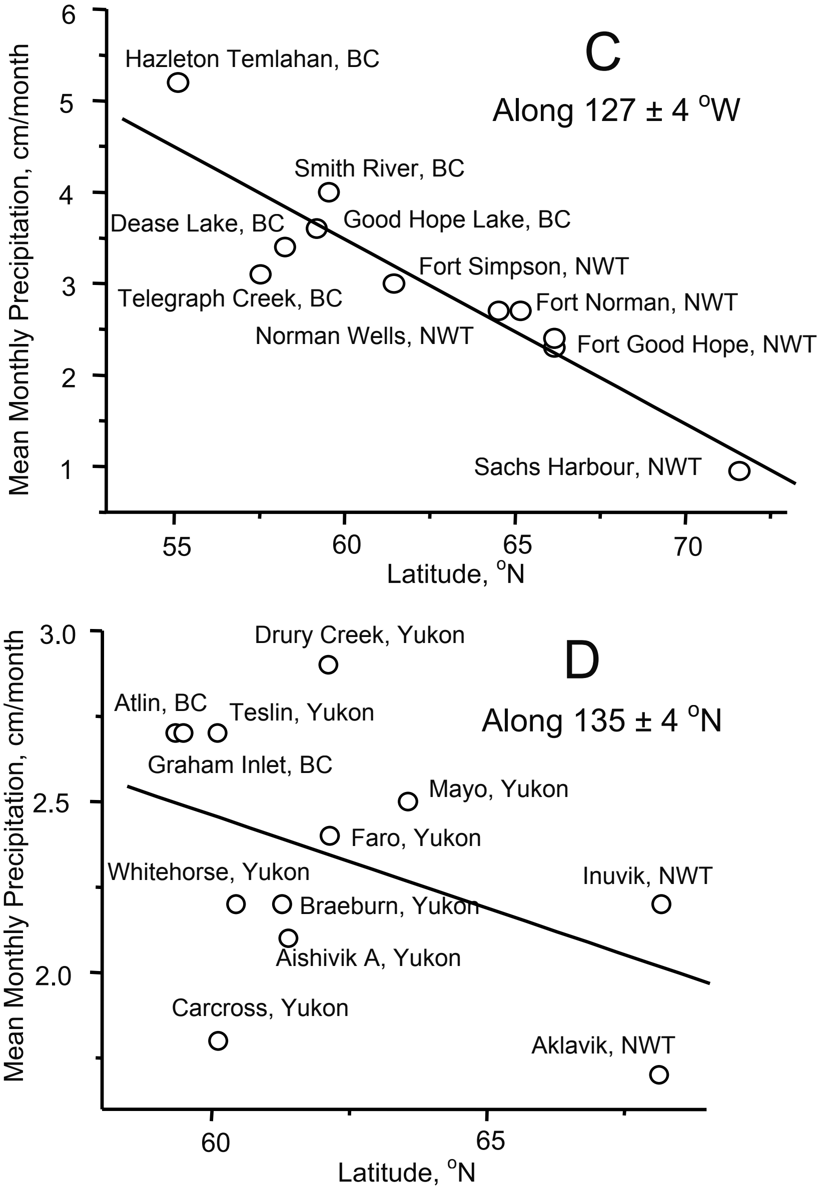

Figure 8 C and D. Monthly averaged total atmospheric precipitation (rainfall and snowfall) vs. northern latitude in Canada.

Table 4. Atmospheric fluxes of Pb-210 in the northern hemisphere.

Location	Latitude	Longitude	Type of Sampling	Pb-210 flux, Bq m^{-2} yr^{-1}	References
1	**2**	**3**	**4**	**5**	**6**
Hazen Lake, NV, Canada	81°45’ N	71°30’ W	Soil profile	7	This study
Camp Century, Greenland	77°10’ N	61°00’ W	Glaciers	15	Turekian et al. 1977
Site 2, Greenland	76°59’ N	56°04’ W	Glaciers	18	Turekian et al. 1977
Lac Belot, NWT, Canada	66°54’ N	126°18’ W	Soil profile	50	This study
Saqvaqjuac, NV, Canada	63°30’ N	90°30’ W	Soil profile	60	This study
Moscow, Russia	55°45’ N	37°42’ W	Artificial collecting system	115	Turekian et al. 1977
Cumbria, England	56°30’N	3° W	Soil profile	162	Eakins et al. 1984
Trout Lake, ON, Canada	51°12’ N	93°18’ W	Soil profile	160	This study
Mirwart, Belgium	50°03’ N	5°16’ E	Artificial collecting system	159	Turekian et al. 1977
Mirwart, Belgium	50°03’ N	5°16’ E	Artificial collecting system	130	Turekian et al. 1977
ELA, ON, Canada	49°N	93°W	Soil profile	150	This study
Seattle, USA	48°N	123°W	Artificial collecting system	108	Shell 1977
Washington coast, USA	47°N	124°W	Soil profile	122	Carpenter et al. 1981
Great Lakes	40-45 °N		Artificial collecting system	183	Robins, 1982
Island, CT, USA	41°30’ N	73°W	Artificial collecting system	133	Lewis 1977
Island, CT, USA	41°30’ N	73°W	Soil profile	124	Lewis 1977
Steam Mill, PA, USA	41°32’ N	78°10’ W	Soil profile	150	Nozaki et al. 1978
Cook Forest, PA, USA	41°20’ N	79°13’ W	Artificial collecting system	167	Lewis 1977
Branford, CT, USA	41°03’ N	73°W	Artificial collecting system	167	Lewis 1977
Branford, CT, USA	41°03’ N	73°W	Soil profile	156	Lewis 1977
New Haven, CT, USA	41°18’ N	72°55’ W	Soil profile	153	Turekian et al. 1977

Table 4. Continued

1	**2**	**3**	**4**	**5**	**6**
Branford, CT, USA	41°20’ N	73° W	Salt marsh profile	167	Turekian et al. 1977
Limestone Run, PA, USA	40°57’ N	76°58’ W	Soil profile	133	Nozaki et al. 1978
New York, NY, USA	40°44’ N	74°00’ W	Artificial collecting system	231	Fisenne et al. 1980
Harrisburg, PA, USA	40°18’ N	76°49’ W	Soil profile	156	Lewis 1977
Boulder, CO, USA	40°00’ N	105°15’ W	Artificial collecting system	133	Moore & Poet 1976
Boulder, CO, USA	40°00’ N	105°15’ W	Soil profile	266	Moore & Poet 1976
Maryland, USA	39° N	76°30’ W	Soil profile	187	Lewis 1977
Maryland, USA	39° N	76°30’ W	Artificial collecting system	200	Lewis 1977
Santa Fe, NM, USA	35°47’ N	105°46’ W	Soil profile	217	Nozaki et al. 1978
Srinagar, India	34°06’ N	74°55’ E	Artificial collecting system	182	Joshi et al. 1967
Dehli, India	28°45’ N	77°20’ E	Artificial collecting system	133	Joshi et al. 1967
Gangtok, India	27°12’ N	88°23’ E	Artificial collecting system	230	Joshi et al. 1967
Calcutta, India	22°34’ N	88°25’ E	Artificial collecting system	102	Joshi et al. 1967
Nagpur, India	21°12’ N	79°04’ E	Artificial collecting system	102	Joshi et al. 1967
Bombay, India	18°57’ N	72°55’ E	Artificial collecting system	250	Joshi et al. 1967
Bangalore, India	12°57’ N	77°30 E	Artificial collecting system	82	Joshi et al. 1967
Ootacamund, India	11°23’ N	76°40’ E	Artificial collecting system	87	Joshi et al. 1967

Estimation of the atmospheric Cs-137 fallout over the lakes investigated was based on the exponential and linear regression of the data experimentally observed in the northern hemisphere (HASL-329, EML-412). Since the sediments in lakes were taken in 1987 - 1993, all Cs-137 data were decay-corrected to 1990. Atmospheric Cs-137 fallout data are plotted against the northern latitude in Fig. 9. Noteworthy, the stratospheric source (Cs-137) and the terrestrial source (Pb-210) have similar fallout patterns. Latitudinal distribution of atmospheric Cs-137 fallout, $I_{\mathrm{Cs\text{-}137}}$ (Bq cm^{-2}), above 40 $^{\circ}$N could be described by the following regression equations:

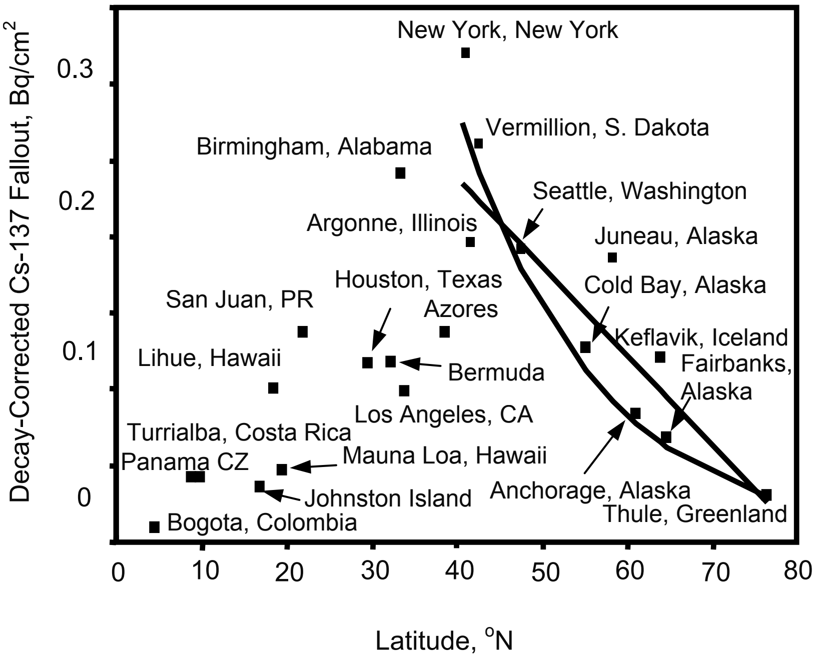

Figure 9. Latitudinal distribution of Cs-137 atmospheric fallout in the northern hemisphere.

(i) exponential regression

$$I_{\mathrm{Cs\text{-}137}} = 3.39 \exp(-0.062\, N),\ r^2 = 0.66,\ n = 12 \qquad \text{(Eq. 15)}$$

(ii) linear regression

$$I_{\mathrm{Cs\text{-}137}} = 0.47 - 0.006\, N,\ r^2 = 0.81,\ n = 9 \qquad \text{(Eq. 16)}$$

Values of atmospheric Cs-137 fallout calculated by Eqs. 15 and 16 are presented in Table 6.

3.2.3. *Evaluation of determined focusing factors*

Focusing factors for the lake sites studied are presented in Table 5 and 6. Since only a small contribution of radionuclides originates from watershed transfer and from *in situ* decay of parent radionuclides (Krishnaswami and Lal 1978), all focusing factors were calculated by dividing measured Pb-210 fluxes to the sediments or Cs-137 sediment inventories (Table 2) by the corresponding measured or theoretically predicted Pb-210 atmospheric fluxes (Table 5) or Cs-137 decay-corrected fallout (Table 6). Mean focusing factors from Pb-210 data, $F_{\text{Pb-210}}$, were averaged with those estimated using (i) Pb-210 concentration in surface air, (ii) experimental and (iii) theoretical Pb-210 atmospheric fluxes. Mean focusing factors from Cs-137 data, $F_{\text{Cs-137}}$, were averaged with those obtained using either exponential or linear regressions.

Noteworthy, all the theoretically predicted values of $F_{\text{Pb-210}}$ correspond well to those experimentally determined from soil profiles.

It can be seen from Tables 5 and 6 that in stratigraphically normal cores (ratio of Cs-137 total activity to total excess Pb-210 ranges from 0.4 to 0.6) focusing factors estimated from Pb-210 data are very close to those estimated from Cs-137 data. The largest difference 32.5 % is found for Lake 375. Values of $F_{\text{Cs-137}}$ are usually larger than $F_{\text{Pb-210}}$ by 1.2 - 1.3 times, with exceptions of lakes Far (core A) and Belot (cores BEL1 and BELBC). This could be caused by an underestimation of the theoretically predicted Cs-137 atmospheric fallout by 20 - 30 %. For all lakes studied, the values of $F_{\text{Pb-210}}$ or the value averaged from $F_{\text{Pb-210}}$ and $F_{\text{Cs-137}}$ could be used for evaluation of the areal-corrected fluxes of atmospheric pollutants.

In the cores with $R_{Cs/Pb}$ less than 0.3 (Hawk Lake, core A; Amituk Lake, core A; Sophia Lake, box cores A and B), $F_{\text{Cs-137}} < F_{\text{Pb-210}}$. In these cases, the anomalous behavior of Cs-137 in the sediments could be due to loss of the surface material prior to or during coring (Robbins et al. 1990). It preferably reduces total Cs-137 as compared to excess Pb-210. This is in agreement with the absence of a subsurface maximum in the Cs-137 profiles in lakes Sophia and Amituk, although it would be expected from the Pb-210

Table 5. Focusing factors in the lakes investigated from Pb-210 data.

Lake, core	Regional atmospheric fluxes of Pb-210, Bq m^{-2} yr^{-1}						Focusing factor using Pb-210 fluxes from:				
	From soil profiles	Theoretically predicted from world-wide data					Soil profiles (col. 2)	Theoretically predicted using data			Mean value from soil profiles and theoretical data Mean ± SD
		Calculated by Equation 10			Estimated by regression analysis of data in Table 4			[Pb-210] in surface air, Bq/1000m^3 (col. 5)	From regression analysis		
		[Pb-210] in surface air, Bq/1000m^3	Precipitations (rainfall+snowfall) cm/month	Pb-210 flux	Exponential regression	Linear regression			Col. 6	Col. 7	
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Lake 375:											
Box core A	150	0.46	5.3	175	156	166	2.16	1.85	2.08	1.95	2.01 ± 0.14
Lake 382:											
Box core 1	150	0.46	5.3	175	156	166	2.07	1.77	1.99	1.87	1.92 ± 0.13
KB core A	150	0.46	5.3	175	156	166	1.93	1.66	1.86	1.75	1.80 ± 0.12
KB core B	150	0.46	5.3	175	156	166	1.87	1.60	1.79	1.69	1.74 ± 0.12
KB core C	150	0.46	5.3	175	156	166	1.53	1.31	1.47	1.39	1.43 ± 0.10
KB core E	150	0.46	5.3	175	156	166	1.93	1.66	1.86	1.75	1.80 ± 0.12
KB core G	150	0.46	5.3	175	156	166	1.45	1.25	1.40	1.31	1.35 ± 0.09
KB core L	150	0.46	5.3	175	156	166	1.81	1.55	1.74	1.63	1.68 ± 0.12
KB core O	150	0.46	5.3	175	156	166	1.25	1.07	1.20	1.13	1.16 ± 0.08
KB core P	150	0.46	5.3	175	156	166	0.93	0.80	0.90	0.84	0.87 ± 0.06
KB core Q	150	0.46	5.3	175	156	166	1.23	1.05	1.18	1.11	1.14 ± 0.08
Green Lake:											
GL4	160	0.45	5	163	141	153	0.74	0.84	0.77	0.77	0.78 ± 0.04
GL5	160	0.45	5	163	141	153	1.79	1.75	2.03	1.87	1.86 ± 0.12

Table 5. Continued

1	2	3	4	5	6	7	8	9	10	11	12
GL10	160	0.45	5	163	141	153	2.24	2.20	2.54	2.34	2.33 ± 0.15
Linge:											
LL1	160	0.45	5	163	141	153	1.29	1.26	1.46	1.35	1.34 ± 0.09
LL2	160	0.45	5	163	141	153	2.51	2.47	2.85	2.63	2.62 ± 0.17
Musclow:											
ML1	160	0.45	5	163	141	153	3.95	3.88	4.48	4.13	4.11 ± 0.27
Orange:											
OL1	160	0.45	5	163	141	153	1.31	1.28	1.48	1.37	1.36 ± 0.09
OL2	160	0.45	5	163	141	153	1.28	1.26	1.45	1.34	1.33 ± 0.09
Sydney											
SL1	160	0.45	5	163	141	153	2.50	2.45	2.84	2.61	2.60 ± 0.17
Trout:											
TL1	160	0.45	5	163	141	153	0.80	0.79	0.91	0.84	0.84 ± 0.05
TL3	160	0.45	5	163	141	153	5.69	5.58	6.45	5.95	5.92 ± 0.39
TL4	160	0.45	5	163	141	153	0.89	0.88	1.01	0.93	0.93 ± 0.06
TL5	160	0.45	5	163	141	153	2.08	2.04	2.36	2.18	2.17 ± 0.14
TL10	160	0.45	5	163	141	153	1.77	1.74	2.01	1.85	1.84 ± 0.12
TL12	160	0.45	5	163	141	153	2.53	2.48	2.87	2.65	2.63 ± 0.17
Nipigon:											
KB core 1	--	0.46	5.3	175	156	166	--	2.57	2.99	2.81	2.79 ± 0.21
KB core 3	--	0.46	5.3	175	156	166	--	2.50	2.92	2.74	2.72 ± 0.21
KB core 4	--	0.46	5.3	175	156	166	--	2.44	2.74	2.57	2.58 ± 0.15
					Fox:						
FOX1	--	0.35	2.4	64	59	66	--	0.94	1.02	0.91	0.96 ± 0.06

Table 5. Continued

1	2	3	4	5	6	7	8	9	10	11	12
FOX2	--	0.35	2.4	64	59	66	--	0.73	0.80	0.71	0.75 ± 0.05
Kusawa:											
KUS1	--	0.36	2.4	67	64	69	--	0.97	1.02	0.94	0.98 ± 0.04
Laberge:											
LAB1	--	0.36	2.4	66	61	67	--	1.18	1.28	1.16	1.21 ± 0.06
LAB2	--	0.36	2.4	66	61	67	--	1.03	1.11	1.01	1.05 ± 0.05
LAB3	--	0.36	2.4	66	61	67	--	1.27	1.38	1.25	1.30 ± 0.07
LAB4	--	0.36	2.4	66	61	67	--	1.18	1.28	1.16	1.21 ± 0.06
Little Atlin:											
LAT1	--	0.36	2.4	67	64	69	--	1.76	1.84	1.71	1.77 ± 0.07
LAT2	--	0.36	2.4	67	64	69	--	1.12	1.17	1.09	1.13 ± 0.04
Far:											
Box core A	60	0.33	2.2	56	50	60	2.33	2.50	2.80	2.33	2.49 ± 0.22
Box core B	60	0.33	2.2	56	50	60	1.97	2.11	2.36	1.97	2.10 ± 0.18
Hawk:											
Box core A	60	0.33	2.2	56	50	60	2.13	2.29	2.56	2.13	2.28 ± 0.20
Box core B	60	0.33	2.2	56	50	60	2.75	2.95	3.30	2.75	2.94 ± 0.26
Amituk											
KB core A	--	0.23	1.0	17	19	25	--	10.59	9.47	7.20	9.09 ± 1.73
KB core B	--	0.23	1.0	17	19	25	--	10.41	9.32	7.08	8.94 ± 1.70
Sophia:											
Box core A	--	0.23	1.0	17	19	25	--	5.29	4.74	3.60	4.54 ± 0.86
Box core B	--	0.23	1.0	17	19	25	--	5.12	4.58	3.48	4.39 ± 0.84

Table 5. Continued

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
KB core A	--	0.23	1.0	17	19	25	--	4.71	4.21	3.20	4.04 ± 0.77
KB core B	--	0.23	1.0	17	19	25	--	4.12	3.68	2.80	3.53 ± 0.67
Hazen:											
Box core A	7	0.16	0.9	11	11	4	2.00	1.27	1.27	3.50	2.01 ± 1.05
Belot:											
BEL1	50	0.3	2.1	48	37	49	2.18	2.27	2.95	2.22	2.41 ± 0.37
BEL2	50	0.3	2.1	48	37	49	1.20	1.25	1.62	1.22	1.32 ± 0.20
BELBC	50	0.3	2.1	48	37	49	2.06	2.15	2.78	2.10	2.27 ± 0.34
Colville:											
COL1	50	0.3	2.1	48	37	49	1.00	1.04	1.35	1.02	1.10 ± 0.17
COL2	50	0.3	2.1	48	37	49	1.38	1.44	1.86	1.41	1.52 ± 0.23

profiles. In these sediments, the Cs-137 activity gradually decreases with depth from the sediment-water interface (data are not shown). The extent of penetration of Cs-137 is shallow (depth of 2-3 cm). The surface sediments are highly compacted (mean porosities in the upper 5 cm ranging from 0.80 - 0.86). Loss of surface material can also cause differences in ω determined from Pb-210 and Cs-137 data.

The condition $F_{\text{Cs-137}} < F_{\text{Pb-210}}$ holds for various cores and types of corers, which points to the possibility that lower Cs-137 inventories are not sampling artifacts. An alternative explanation is that Lake Sophia and probably Lake Amituk, contain hypersaline waters in the monimolimnia. In this case, Cs-137 bound by particulate matter could be replaced in sediments by cations present in saline water. Lakes Amituk and Sophia have high focusing factors. It should be noted that Lakes Amituk and Sophia have large drainage area to lake area ratios, 38.9 and 18.5 respectively. Along with that, combination of two factors, extensive ice cover and existence of a hypersaline water layer in the monimolimnia, could create better opportunities for settling of very fine particulates in the deepest parts of the lakes and, thus, for sediment focusing. Lakes Hawk and Far contain soft water. Presence of soft water may cause the enhanced mobility of Cs-137 in sediment and, hence, the depletion of Cs-137 inventory.

In another anomalous cores with $R_{Cs/Pb} > 0.6$ (Lake Nipigon, cores 1 and 2; Lake Laberge, cores LAB1 and LAB3; Little Atlin Lake, core LAT2; Lac Belot, core BEL2 and Lake Hazen), the relationship $F_{\text{Cs-137}} > F_{\text{Pb-210}}$ holds. All these lakes are large with significant watershed areas. The enhanced input of Cs-137 from the watershed, especially during period of snow and ice melting, may increase the total Cs-137 inventory as compared to excess Pb-210. For all anomalous cores, as a first approximation, the values of $F_{\text{Pb-210}}$ should be preferably adopted.

4. CONCLUSIONS

Fifty-four sediment cores from 20 Canadian lakes Canada have been collected and analyzed by Pb-210 and Cs-137 techniques. The strategy was to estimate several depositional characteristics of lake sediments, which are necessary for monitoring and forecasting of environmental pollution. The study of excess Pb-210 and Cs-137 activity distributions in lake sediments revealed the following:

(1) Pb-210 and Cs-137 dating techniques could be used for reconstruction of histories of chemical contamination in Canada, including the high Arctic zone, over the past 150 years.

(2) Mass sedimentation rates in undisturbed cores, estimated from Pb-210 data using combinations of three and, sometimes, four models, agree well within the range of experimental error. In general, Cs-137 data do not yield meaningful values of mass sedimentation rates because of mixing and post - depositional mobility of Cs-137 in sediments.

Table 6. Focusing factors in the lakes investigated from Cs-137 data.

Lake, core	Atmospheric Cs-137 fallout, Bq cm^{-2}		Focusing factor from Cs-137 data:		
	Exponential regression	Linear regression	From exp. regression	From linear regression	Mean value
1	**2**	**3**	**4**	**5**	**6**
Lake 375:					
Box core A	0.156	0.182	3.21	2.75	2.98
Lake 382:					
Box core 1	0.156	0.182	2.17	2.53	2.35
Nipigon:					
KB core 1	0.156	0.182	7.56	6.48	7.02
KB core 3	0.156	0.182	5.00	4.29	4.64
KB core 4	0.156	0.182	5.13	4.40	4.76
Fox:					
FOX1	0.076	0.114	1.39	0.93	1.16
FOX2	0.076	0.114	1.18	0.79	0.99
Kusawa:					
KUS1	0.081	0.12	1.40	0.94	1.17
Laberge:					
LAB1	0.078	0.117	3.21	2.14	2.67
LAB3	0.078	0.117	2.51	1.68	2.09
Little Atlin:					
LAT2	0.081	0.12	1.98	1.33	1.65
Far:					
Box core A	0.067	0.102	2.33	1.53	1.93
Hawk:					
Box core A	0.067	0.102	1.09	0.72	0.90
Amituk					
KB core A	0.033	0.035	5.09	4.80	4.95
Sophia:					
Box core A	0.033	0.035	1.24	1.17	1.21
Box core B	0.033	0.035	1.06	1.00	1.03
Hazen:					
Box core A	0.022	0	2.91	--	2.91
Belot:					
BEL1	0.054	0.082	2.59	1.71	2.15
BEL2	0.054	0.082	5.56	3.66	4.61
BELBC	0.054	0.082	1.85	1.22	1.54
Colville:					
COL2	0.054	0.082	2.26	1.49	1.87

(3) Pb-210 geochronologies estimated for lake cores, using the RSSM and CFM models are generally in good agreement in undisturbed cores with time- stratigraphic sediment horizons determined from Cs-137 profiles. Geochronological anomalies observed in Cs-137 profiles may be attributed to either mixing or to other type of sediment redistribution processes including post-depositional Cs-137 mobility and sediment focusing.

(4) Areal atmospheric radionuclide fallouts were calculated by two different methods: from Pb-210 concentration in the surface air and from the northern hemisphere - wide measured Pb-210 and Cs-137 atmospheric flux data.

(5) Focusing factors of lake sediments calculated using theoretically predicted areal atmospheric Pb-210 fluxes correspond well to experimentally estimated values. This method of theoretical prediction of atmospheric Pb-210 and Cs-137 fallouts can be used for different location across Canada.

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BIOSENSORS FOR WATER QUALITY MONITORING

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1. INTRODUCTION

At present, the state of the environment is of great concern due to its enormous impact on living organisms and its deteriorating quality as a result of human activity. To bring environmental management to higher qualitative levels and reduce hazardous human impact, the following measures could be taken: (i) improvement of the protection of natural resources, (ii) effective control of the release of potentially dangerous substances into the environment, (iii) localization and treatment of sources of contamination, etc. As various contaminants, such as industrial products, pesticides, insecticides, and surface-active substances, get into water sources, they may create non-favorable conditions for organisms living in that water. As a result, the biological equilibrium in water reservoirs is destroyed and their capacity for self-purification is decreased. In turn, it may lead to harmful impact on human health. Therefore, monitoring of toxic elements in the environment is a high priority for analytical chemists. Unfortunately, most of the available approaches to such monitoring are based on traditional methods, such as chromatography, mass spectroscopy, etc. (Anonymous 1977, 1982, 1983, 1987). These methods have certain disadvantages and limitations since they are based only on physical and chemical principles. Often, they are expensive, labor-intensive, have low sensitivity, and do not readily provide efficient and economical assessment of the ecological situation (Anonymous 1988). The use of living organisms as indicators (Anonymous 1988, Anonymous 1990,

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Tumanov et al. 1981, 1993) may increase the reliability and effectiveness of analytical controls of environmental contamination.

Microorganisms, protozoa, cultures of different tissues, water plants, and animals may serve as such biological indicators (Anonymous 1990, Tumanov et al. 1981, 1993, Rubenchik 1972, Brahinskij 1995). All these organisms are very suitable for indicating total toxicity. At the same time, the determination of group-specific substances necessitates the use of some enzymes, which are sensitive to specific chemical groups of contaminants. Finally, to estimate individual toxins it is necessary to use specific recognizing structures, for example, antibodies.

This article describes the development of various types of biosensors based on electrochemical, optical and thermal transducers, which are intended for use in the control of total toxicity as well as for the simultaneous determination of individual and group-specific low molecular weight toxic elements in the technological processes of water purification.

2. BIOSENSORS FOR THE DETERMINATION OF TOTAL TOXICITY OF ENVIRONMENTAL CONTAMINANTS

Among different living organisms, *Daphnia* (*Daphnia magna St.*) is the most used for the determination of the total toxicity level of environmental contaminants (Sherban' 1988, Brahinskij 2000, Kruhlov and Kirijenko 1985). Previously, we have demonstrated that *Daphnia* culture medium does not produce spontaneous chemiluminescence (ChL), but in the presence of hydrogen peroxide and luminol a ChL signal is emitted (Ivashkevich et al. 2002, Levkovetz et al. 2002). The optimal conditions for ChL measurement were described in (Levkovetz et al. 2003). In special experiments, it was established that the presence of 5 organisms in 10 mL is optimal for the detection of ChL. *Daphnia* is included in the International Register as a living organism, which should be used for water quality testing. Along with *Daphnia*, this Register contains some bioluminescent microorganisms, algae, fish and other living species. We have also developed optical biosensors based on bioluminescent microorganisms (Katzev 2002, Katzev et al. 2003, Katzev and Starodub 2003).

2.1. *Daphnia*-Based ChL Biosensor

To measure the ChL of *Daphnia* culture medium, we created a special computer-controlled device consisting of a photo-multiplier with a measuring cell. A special computer program was created for automatic measurement of the ChL signal, its processing and presentation in a convenient form. It was found that this biosensor is very sensitive to the presence of surface-active substances (SAS) and allows their quantitative measurement at a concentration of about 20 mg/L and less. Higher concentrations of these substances in solution caused almost 100 % toxicity.

This biosensor was utilized in our laboratory for optimization of the water purification process. The detailed description of these studies is given in (Levkovetz et al. 2003, Katzev and Starodub 2003). The following was demonstrated: (i) optimal photoozonation may be achieved if the concentration of substances is decreased by 50 % from the initial one (~50 mg/L, i.e., the most common level of SAS in wastewater); (ii) photo-ozonation is more effective than ozonation or treatment by ultraviolet alone, as was demonstrated in the case of polyoxyethylated nonylphenol (OP-10) destruction (Fig. 1); (iii) the use of active carbon after photoozonation gave a sharp decrease in the toxicity of treated water due to adsorption of some organic radicals and partial decay of SAS; (iv) the content of SAS in water and the water toxicity may be sharply decreased by biodegradation processes (down to 18 mg/L from an initial concentration of 150-200 mg/L).

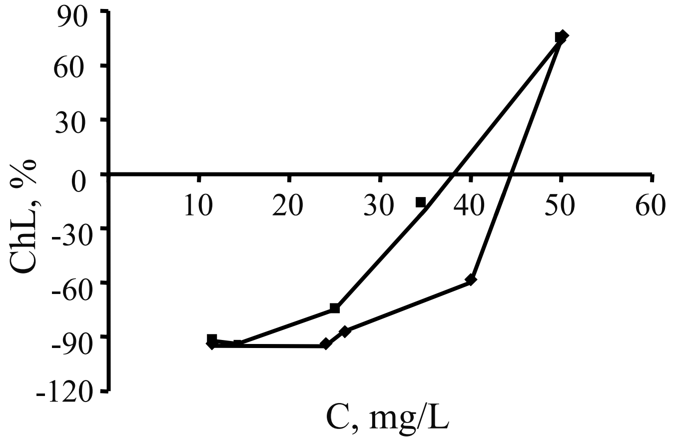

Figure 1. Changes of ChL level of *Daphnia* maintenance medium upon addition of OP-10 samples prepared in distilled water and treated by O_3-UV (diamonds) and O_3 (squares).

The reduction of SAS concentration was accompanied by a decrease in acute toxicity of the reaction mixture. It was confirmed by analysis of morphological and functional changes of *Daphnia*. The presence of H_2O_2 in the *Daphnia* maintenance medium increased the toxicity of some oxidized samples and decreased the ChL intensity.

2.3. Biosensors Based on Bioluminescent Bacteria

For the first time, bacteria removed from the Black Sea and the Sea of Azov and selected according to their sensitivity to SAS and other toxic substances were used for the estimation of general toxicity of water samples. The above-mentioned special computer-controlled device consisting of a photo-multiplier with a measuring cell was utilized for the measurement of the bioluminescent signal in stationary conditions.

The study of the influence of various types of SAS on the intensity of bioluminescence of bacteria (*Photobacterium phosphoreum* K3 (IMB B-7071), *Vibrio fischeri* F1 (IMB B-7070), and *Vibrio fischeri* Sh1 revealed that the majority of substances investigated act as inhibitors of bioluminescence. The analysis of the kinetics of inhibition showed some peculiarities (Fig. 2). Firstly, cationic and anionic SAS showed similar kinetics of inhibition. Secondly, nonionic SAS demonstrates an additional step, where the inhibition was absent and some activation of bioluminescence was observed. Therefore, for assessment of the toxicity of the latter group of SAS, it is necessary to incubate the corresponding substances with bacteria for a longer time.

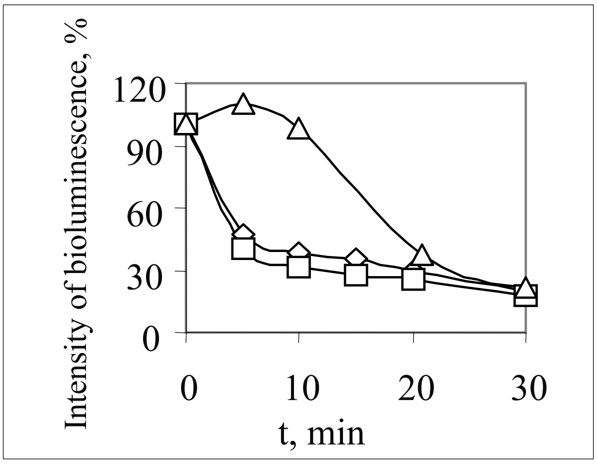

Figure 2. Kinetics of bacterial bioluminescence inhibition by different types of SAS: non-ionic (triangles); anionic (diamonds), and cationic (squares) SAS.

It was revealed that the sensitivity of *V. fischeri* to OP-10 (non-ionic SAS) and sodium alkylbenzolsulphonate (ABS, anionic SAS) could be increased by using some additional factors. In particular, the addition of certain substances modified the sensitivity of the bacteria, optimized their growth and allowed analysis in weakly acid conditions. For example, the addition of 0.5 mg/L analysis in weakly acid conditions. For example, the addition of 0.5 mg/L miramistine decreased the value of EC_{50} by 57-200 times in the analysis of OP-10 (Table 1). It is probable that the increase of sensitivity of the bacteria could be caused by changes in the cell membrane permeability to non-ionic SAS under the influence of miramistine. At the same time, the addition of miramistine did not noticeably influence the sensitivity of the bacteria to ABS. The lack of effect in the case of ABS is probably due to the absence of changes of cell membrane permeability for anionic SAS. It is well known that bacteria have variable sensitivity to toxic agents during different phases of growth. We have tested *V. fischeri F1* during the logarithmic, stationary and later stationary phases of growth. It was found that for analysis of detergents the logarithmic phase is more suitable. In this case, the sensitivity of bacteria to OP-10 and ABS increases by 5-6 and 3-4 times, respectively, as compared with that found for the stationary phase (Table 2).

Table 1. Changes of EC_{50} for OP-10 and ABS upon addition of miramistine to bacteria.

Incubation time, min	EC_{50} for OP-10, mg/L		EC_{50} for ABS, mg/L	
	Control	With miramistine	Control	With miramistine
10	80	1.4	40	45
20	70	1.2	36	42
30	60	0.3	30	40

Table 2. Sensitivity of *V. fischeri F1* to SAS at the logarithmic (1), stationary (2) and later stationary (3) phases of growth.

Incubation time, min	EC_{50} for ABS, mg/L			EC_{50} for OP-10, mg/L		
	Phase of growth			Phase of growth		
	1	2	3	1	2	3
30	10	40	50	16	80	*N/D
60	9	36	45	10	70	*N/D
90	9	30	45	10	60	*N/D

*N/D indicates that EC_{50} were not determined due to low sensitivity of microorganisms used.

The lowest value of pH, at which the bioluminescence of *V. fischeri* F1 is stable, is 5.5. The results of the influence of OP-10 and ABS on the bioluminescence of *V. fischeri* F1 at this pH are given in Fig. 3.

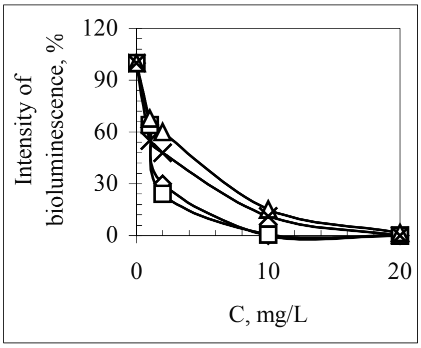

Figure 3. Influence of OP-10 and ABS on the bioluminescence of *V. fischeri* F1 at pH 5.5. OP-10, incubation time 30 min (diamonds); OP-10, 60 min (squares); ABS, 30 min (triangles); ABS, 60 min (crosses).

The preliminary optimal conditions estimated for analysis were used during the determination of the total toxicity of ABS and OP-10 solutions purified by the combined action of O_3 and UV-radiation (Levkovetz et al. 2003, Katzev and Starodub 2003). The results of bioluminescent analysis of ABS solutions before and after their treatment by ozone and UV are given in Table 3. In contrast to untreated solutions of ABS, the solutions after treatment by O_3-UV did not measurably weaken the bioluminescence of the bacteria, provided the level of SAS destruction does not exceed 50%. However, at a residual concentration of SAS of less than 20 mg/L, the inhibition of bioluminescence was decreased by ~ 14%.

Table 3. The level of bacterial bioluminescence in ABS solutions treated by O_3-UV.

Type of treatment	t, min	Dose of absorbed O_3, mg/L	C_{ABS}, mg/L	C_{H2O2}, mg/L	Bioluminescence, %
Initial solution	0	0	50.0	0	9.0
O_3-UV	16.5	3.5	39.9	0	98.9
O_3-UV	82.0	35.9	25.0	2.2	98.9
O_3-UV	160	39.6	19.2	0	85.6
O_3-UV	155	72.1	11.0	6.6	53.5
Control	-	-	-	-	100

Complete destruction of the initial ABS decreased the bioluminescence by ~ 2-fold. Partially, the toxicity of samples increased, probably, as a result of the formation of organic peroxides and/or H_2O_2.

During intensive treatment of OP-10 solutions by O_3-UV, the toxicity of the samples did not increase, even if the level of OP-10 destruction was about 80%. Similar investigations using *Daphnia magna* have shown that, during the oxidative destruction of OP-10 solutions by O_3-UV, the toxicity of the solutions essentially decreased. A totally different level of toxicity was observed after filtration of the partially oxidized solutions of SAS through biologically activated carbon (BAC). After contact of such solutions with carbon activated by special biodegradable bacteria for 15-60 min, the level of their toxicity sharply decreased (Table 4).

Thus, similar to the *Daphnia* based biosensor, the use of bacterial bioluminescence for testing of anionic and non-ionic SAS has shown that the partial destruction (up to 50% of the initial concentration) of these substances by an O_3-UV combination is not accompanied by an increase in the total toxicity of the treated samples. Such destruction of SAS is acceptable for subsequent biological sorption, which sharply decreases the total toxicity of purified water.

Table 4. The level of bacterial bioluminescence of ABS solutions treated by O_3-UV and filtered through BAC.

Type of treatment	*t*, min	Dose of absorbed O_3, mg/L	C_{ABS}, mg/L	pH	Bioluminescence (%)		
					pH 7.0	pH 5.5	pH 5.5*
O_3-UV (input water)	155	72.1	4.0	4.9	53.5	-	-
BAC	30	-	0	6.8	105.8	105.0	102.0
BAC	50	-	0	7.0	103.2	108.0	95.5
BAC	100	-	0	7.4	122.6	88.0	92.3

* at a dilution of 1:2.

The use of bacterial bioluminescence for testing the toxicity of anionic and non-anionic SAS at pH 7.0 has shown that their partial destruction (up to 40-50% of initial concentration) by ozone or by the combination of ozone with UV-radiation is not accompanied by an increase of toxicity of the reaction mixture. Thus, this treatment is acceptable for the next step of water purification using biodegradable microorganisms. The combination of preliminary oxidation with adsorption on BAC allows complete elimination of toxicity associated with the presence of SAS and the products of their destruction in water.

2.4 Thermal Biosensor

The detailed analysis of recent scientific literature and patents allows one to conclude that biosensors based on microelectronic transducers are the most perspective among the others. At present, a number of leading firms are searching for new materials, which could be used in microelectronics. Integral devices based on silicon are at the limit of miniaturization and further decrease of their dimensions is not physically possible. The next step towards miniaturization could be associated with employment of solid electrolytes. Due to their unique abilities, solid electrolytes serve as a basis for a variety of devices, such as batteries, fuel elements, electro-chromic displays, thermoelectric devices, memory elements, etc. They are able to withstand changes of external electrical and magnetic fields, to work in a wide range of temperatures; they are long-lived and may be stored for a very long time without any loss of their main characteristics. Recently, a new material, $LaLiTiO_3$, was synthesized. It is a solid electrolyte with high ionic conductivity. This material in ceramic form was studied as a dielectric, for example, for application in microwave techniques. However, thin films of this material have not been studied.

Thermobiosensors (TBS) are based on thermochips (e.g., thermistors, thermoelements) to measure changes of heat, which is produced during enzymatic, immune and metabolic reactions. It is well known that about 78 kJ per millimole of reactants may be produced during enzymatic, immune and metabolic reactions (Kul'berg 1985, Bevza et al. 2002). TBS could be widely used in medical diagnostics, environmental monitoring and for the control of various biotechnological processes.

One of our main objectives was the development of a technology for obtaining thin films from solid electrolytes and the study of their characteristics. The next step was the design of a thermochip, which could be used in thermal biosensors for the determination of glucose, urea, and some SAS in aqueous solution.

2.4.1. Formation of Solid Electrolyte Thin Films Containing β-Al_2O_3 and $LaLiTiO_3$

Most dielectric and semiconductor rare earth compounds are able to sublime during heating in vacuum and form amorphous films on a neutral surface. Film formation is accomplished by a vapor-solid transition. This process completely corresponds to the well known theory of nucleation, and includes the following steps: (i) adsorption of atoms and molecules; (ii) achievement of critical dimensions of "nucleus"; (iii) growth of "nuclei" up to supercritical dimensions and appearance of new ones; (iv) formation of some islands from “nuclei”, and (v) extension and coalescence of islands and transformation of second generation “nuclei” into the solid film.

The deviations from the above general scheme are manifested as the formation of “nuclei” with smaller critical dimensions than those typical for well-known rare earth compounds and solid finely dispersed films. For example, the “nuclei” of aluminum oxide film have dimensions of more than 4 nm but germanium monoxide “nuclei” are 9 nm and neodymium oxide “nuclei” do not exceed 2 nm. At the same time, “nuclei” of neodymium oxide on a solid support are more rounded and thick than those of silicon, aluminum and germanium monoxides. This promotes the formation of finely dispersed films with small critical thickness. It was experimentally established that the upper critical temperature of the solid support (T_c), below which the rare earth compounds are condensed, is about $2.3T_e$, where T_e is the temperature of substance evaporation. The determination of the lower critical temperature was unsuccessful.

The dimensions of “nuclei” depend on the rate of their formation. The optimal temperature for deposition of rare earth compounds on the solid support is found to be $0.1T_e$. Increase of temperature leads to small “nuclei” and to a decrease of probability of “nuclei” formation. The optimal temperature of the solid support ranges from $0.05\text{-}0.15T_e$. The formation of finely dispersed films from oxides of rare earth compounds occurs at the rate of deposition more than 0.1 nm/s. Nevertheless, it is necessary to mention that maintaining the high rate of evaporation of rare earth compounds is extremely difficult. In practice, the evaporation of the rare earth compounds is conducted at 0.5 nm/s. It decreases a degree of substance dissociation and activates the oxidization of lower oxides and metals formed as a result of dissociation. The latter strongly depends on the level of vacuum in the working chamber, in particular, on the partial pressure of oxygen.

Method of explosive evaporation. The best results for deposition of layers from powdery mixtures were obtained by the method of explosive evaporation. The method is based on instantaneous evaporation of very small quantities of substances or mixtures. The device includes a vibrator bunker, containing a finely dispersed powder of the substance to be evaporated, and a tungsten evaporator. The powder is fed to the heated evaporator by vibration. As a result, a number of rapid explosions of very small quantities of powder occurs forming a homogenous vapor. This microdosing allows formation of thin films having a thickness of a few atomic layers. This method is used for the formation of films from compounds having different evaporation pressure. There is no need to precisely control the vapor pressure or temperature of the evaporator. In reality, control of film ingredients is achieved by complete evaporation of small quantities dosed in appropriate ratios. In many cases, the vapor landing on the support is supersaturated and the film composition does not depend on the coefficient of condensation. To obtain films based on rare earth compounds, the selection of materials and design of the evaporator are both of great importance. The material should not interact with the evaporated compounds and it should be stable at a temperature of more than 2000°C. The simplest version of evaporator is a tungsten tape of thickness 125 μm.

Method of magnetron dispersion. An anomalous glowing discharge, produced in the magnetron-dispersed systems (MDS), takes place in electric and magnetic fields. Electrons emitted from the target under the influence of ionic bombardment are trapped by the magnetic field. They perform a cyclic motion along a closed trajectory near the target surface. Due to multiple collisions of electrons with atoms of the plasma-forming gas (usually argon), the degree of plasma ionization sharply increases and the density of ionic current rises (by approximately 100-fold as compared to diode dispersion systems without a magnetic field). As a result, the rate of dispersion of the target material increases by 50-100 times. Depending on the strength of the magnetic induction in the MDS, three types of working regime may be observed. If the magnetic field is weak, a regime with a predominantly positive space charge at the cathode is taking place occurs. At a medium level of magnetic induction, a regime with negative space charge at the anode, where the main part of the applied voltage drops, occurs. In strong magnetic fields, the regime with the anodic voltage drop is partially modified and again the voltage drop in DKA becomes considerable.

The transition between regimes depends on the strength of magnetic induction, the design of the MDS, the pressure of the plasma-forming gas, etc. Since magnetic induction increases the velocity of electron motion, the number of their collisions with atoms of plasma-forming gas simultaneously increases, i.e., the action of a magnetic field is similar to an increase of gas pressure.

The most important parameters of the deposition process, which exert a strong influence on the properties of films formed, are as follows: (i) power of the discharge, (ii) the pressure of plasma-forming gas, (iii) length of time of deposition, (iv) temperature of pre-heating of both the working and reverse sides of the plates, (v) the bias voltage applied to the plate during film deposition. In addition, rotation of the plate during deposition affects the uniformity of condensate on it. The rate of film deposition depends on the power applied. Partially, the power of the discharge, at constant output, depends on the pressure of plasma-forming gas. The desired rate of film deposition in MDS may be influenced by discharge current or power input. To achieve reproducibility and stability of film deposition, it is necessary to keep the discharge current and power at relatively constant levels with deviations of not more than ±2% and ±20 W. The deviation of working pressure should be no more than 5%.

The main advantages of MDS are: (i) the universality of the process, allowing the production of metal films, alloys, semiconductors and dielectrics;

(ii) the high rate of deposition (up to several μm/min) and the possibility of its regulation over a wide range; (iii) the preservation of the ratio of the main components in the final deposit; (iv) the high purity of the films; (v) the strong adhesion of the films to the solid support; (vi) the possibility to control the structure and characteristics of the films by changing the parameters of the deposition; (vii) the low porosity and very thin films; (viii) the low effects of radiation and heat on the structure of deposits; (ix) the possibility of carrying out the process in reactive conditions of discharged gas that produces films of nitrides, carbides, oxides and other substances; (x) the high energy efficiency of the process; (xi) the possibility of mathematical description of the process and its subsequent control by special microprocessors; (xii) the reversibility of the process allowing its use for deposition and also etching of a number of materials; (xiii) the possibility of automation.

The main disadvantages of MDS are: (i) the relatively low coefficient of utilization of target materials (about 25% for flat targets), which necessitates an increase in complexity of target form or design of the magnetic system; (ii) the comparatively high irregularity of thickness of perceptible film due to dispersion of material from the narrow erosion zone having the form of a ring or ellipse; (iii) the appearance of heavy-current arcs on the target surface or between target (cathode) and anode as a result of structural irregularities and the presence of oxide films and contaminants on the target surface, which destabilizes the deposition process and worsens the quality of films formed; (iv) the formation of currents of highly energetic electrons that supply the principal (up to 60%) thermal load to the solid support; (v) the presence of a stream of reflected and neutralized argon ions with energy up to 160 eV, which require their thermalization, if film deposition is carried out on the thin insulating layers; (vi) the comparatively high pressure of pure plasma-forming gas (0.3-1.5 Pa) to prevent contamination of the film.

2.4.2. Method of Film Preparation

The preliminary selected silicon plates were treated by solution containing H_2O_2 and HCl at the temperature of 80°C for 10 min. Then, after rinsing using deionized water and drying in centrifuge, they were treated by solution consisted of H_2O_2 and NH_4OH, washed by deionized water and dried in centrifuge. After that, silicon was thermally oxidized at 960°C in three consecutive steps: 1) in dry oxygen for 20 min; 2) in humid oxygen for 40 min and 3) in dry oxygen for 20 min.

Method of explosive evaporation. Thin films of β-Al_2O_3 were obtained by explosive evaporation using the WUP-5 device. A finely crushed powder (1-2 g) of the required compounds, previously dried at 300°C for 15 min, in an appropriate ratio was placed in the sampler. Plates of oxidized silicon or glass ceramic were used as solid support. They were secured inside the vacuum chamber by special holders. Both plates contained a comb-type contact grating. The sampler was positioned in such way that its nozzle was placed under the 125-μm thick tungsten strip evaporator. The plates were placed facedown above the evaporator. Then, the vacuum in the chamber was established at 5x10^{-6} mm of Hg and the plates were heated up to temperature (160, 200, or 240^{o}C) during 10-15 min. After that, the sampler was switched on starting the evaporation. After switching off the sampler, the solid support was annealed for 10-15 min. The solid support with the deposited film was cooled down for 15 min while vacuum was maintained. The deposition of β-Al_2O_3 films onto oxidized silicon plates required 20-30 min and a solid support temperature of about 160^{o}C.

Method of magnetron dispersion. Thin films of $LaLiTiO_3$ were obtained by magnetron dispersion on the oxidized silicon plate and glass ceramic with contact grating in the form of a terminal strip. The distance between target and support was 50 mm. The parameters were: argon pressure of 10^{-2} mm of Hg, dispersion power 70 W, temperature of support 40-50^{o}C, displacement on the support 20 V.

The contacts were deposited on thin samples by electron beam evaporation of Ti (V=12 kV, emission current 160 mA, dispersion time 15 min, d=0.4 μm).

2.4.3 Design of Thermoelement

The design of the multi-layer thin film thermotransducer is shown in Fig. 4. To decrease the influence of ambient temperature, the prepared thermoelement was placed in a special heat-insulating reservoir.

2.4.4 Experimental Technique

The measurements were conducted using the calibrated thermotransducer at temperatures ranging from -10 to 70^{o}C with increments of 5°C. The experimental cell for the examination of thermal transducers made of solid electrolytes is presented in Fig. 5.

2.4.5 Determination of Thermoelectrical Characteristics

The principal scheme for measuring the thermo *emf* in films of $LaLiTiO_3$ and β-Al_2O_3 is shown in Fig. 6. The measuring device includes three resistive chips (2, 3 and 4), and one of them (4) is used as a heated element. The underside of chip 2 is glued to the heated element 3 by a special thermoconductive glue. The heated element is connected to the DC power source. The resistance of the cooled and heated ends of the chip was registered and converted into temperature readings by a digital device. The

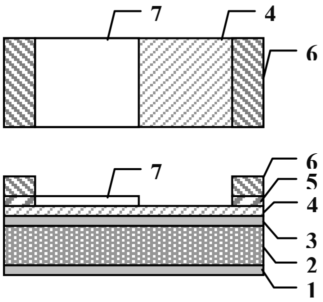

Figure 4. Design of the thin film thermal transducer: 1-SiO_2, 2–Si, 3–SiO_2, 4–β-Al_2O_3 (or $LaLiTiO_3$), 5–Ti, 6–Ni, 7–Al_2O_3.

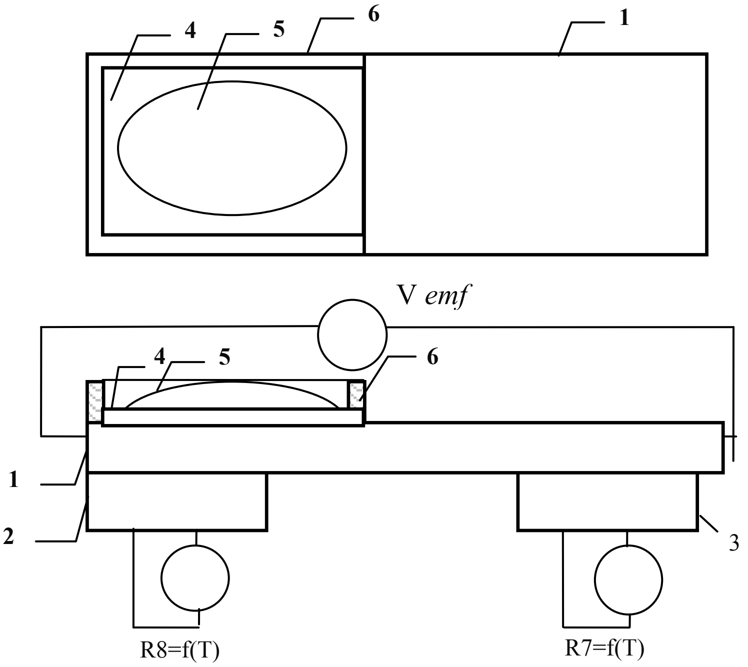

Figure 5. Experimental cell for examination of solid electrolyte biosensor films. 1-solid electrolyte film, 2–thermoresistive chip of heated end of biosensor, 3- thermoresistive chip of cooled end of biosensor, 4–Al_2O_3, 5–biochemical element and 6–silicon organic compound (KO-85).

measuring system contains two autonomic channels that allow changes of *emf* values to be measured independently of the temperature of the effective zone of the heated film.

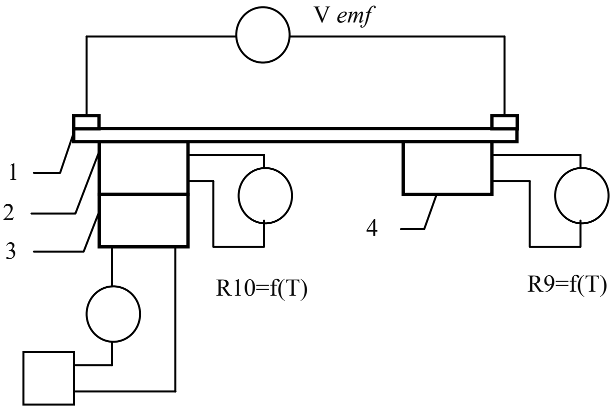

Figure 6. Principal scheme for measuring the thermo *emf.* 1–tested sample, 2–heated end of the chip, 3–heated element, 4–cooled end of the chip, 5–power source.

2.4.6. Characteristics of Thermoelements and Enzymatic Biosensors

In the case of $LaLiTiO_3$ films, the character of the temperature-dependence of electric resistance is similar to that of semiconductor materials. It has an exponential dependence on the negative temperature coefficient that allows thin electrolyte films to be considered as semiconductors with mixed electronic-ionic conductivity. For thin films of β-Al_2O_3, this dependence is practically linear with negative temperature coefficient of resistance in the range of temperature from –60°C to +80°C. It is stipulated by simultaneous action of several thermoactivating mechanisms. The maximum value of thermo *emf* for $LaLiTiO_3$ films is 209 μV/ °C and it is 6-8 times higher compared to semiconductor thermoelements within the above temperature range.

Immobilized β-glucose oxidase on the surface of a thermistor based on $LaLiTiO_3$ films, registered a thermo *emf* of about 45 μV in the presence of 100 mM/L glucose. If urease was used as the sensitive biological structure, a response of about 160 μV in the presence of 100 mM/L urea was observed.

2.4.7 Cell Thermal Biosensor and Water Quality Control

For control of very strong total toxicity caused, for example, by a combination of detergents and different toxic by-products formed at the intermediate steps of water treatment by ozone and UV-radiation, we developed thermal microbial biosensors based on *Saccharomyces cerevisiae* and *Vibrio fischeri* (Fig. 7). These microbial cells were immobilized on the surface of one of the thermistors, whereas another served as a reference. The thermosensitivity of these biosensors is about 0.001°C. Taking into account the low sensitivity of the microbial cells to detergents, both thermal biosensors are only suitable for control of total toxicity of wastewater.

Figure 7. Recording part and sensitive semiconductor unit of thermal biosensor.

The sensitivity of these biosensors to detergent Triton X-100 is about 0.5 mg/mL. Therefore, they are most suitable for control of high level of water toxicity.

3. BIOSENSORS FOR THE DETERMINATION OF GROUP SPECIFIC TOXIC SUBSTANCES AND THEIR INDIVIDUAL COMPONENTS

To determine group-specific toxic substances, for example, phosphororganics, chlororganics, cyanides, etc., we have developed multi-biosensors based on electrolyte-insulator-semiconductor (EIS) structures (Starodub and Starodub 2000, 2001a, 2001b, 2002, 2003, Starodub et al. 2001, Starodub, 2002). This device is very suitable for wide screening of toxic substances in the environment. Its sensitivity is not high but it can conduct simultaneous analysis of a large number of samples. At the same time, to verify the results obtained at the screening stage and to discover the individual components responsible for the toxic effect, we have developed biosensors based on the ion-sensitive field effect transistors (ISFETs) and on surface plasmon resonance (SPR). Some experimental results on utilization of these biosensors for water quality control will be presented below.

3.1. SPR-Based Biosensors

The general view of an SPR-based biosensor is shown in Fig. 8. The measuring part of this biosensor was made in the Institute of Physics of Semiconductors of the Ukrainian National Academy of Sciences. The biosensor was employed for water quality control during purification by

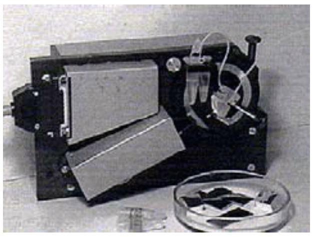

Figure 8. SPR-based immune biosensor.

photoozonation (Levkovetz et al. 2003, Katzev and Starodub 2003). Ethoxylated nonylphenol (NphEO) was used as a model of SAS. The immunoassay was conducted via competitive reaction, as free and conjugated NphEOs competed for specific sites of antibodies immobilized on the transducer surface. The latter were immobilized from antiserum on a gold surface pretreated by polyelectrolytes (Fig. 9) and staphylococcal protein A.

Figure 9. Polyelectrolites: α-poly(alylamine) hydrochloride (PAA) (a) and sodium poly(sterenesulfonate) (b).

The conjugates of NphEO with bovine serum albumin, ovalbumin, soyabean tripsin inhibitor (STI) and the specific polyclonal antibodies to these conjugates were obtained from B. Dzantijev (Institute of Biochemistry of Russian Academy of Sciences) and from N. Piven (Institute of Bioorganic Chemistry of National Academy of Sciences of Belarus).

To provide strong immobilization of the sensitive biological elements on the transducer surface of the biosensor, we formed an intermediate polyelectrolyte layer. At the same time, to orient specific IgG towards the solution, protein A was immobilized on the top of the polyelectrolyte film. Protein A binds to a specific site of IgG, which is situated in the second domain of Fc-fragment. As a result of this interaction, the F(ab)2 fragments of IgG were oriented towards the solution (Fig. 10).

It was found that the sensitivity of the NphEO determination was 1 ng/mL (Fig. 11).

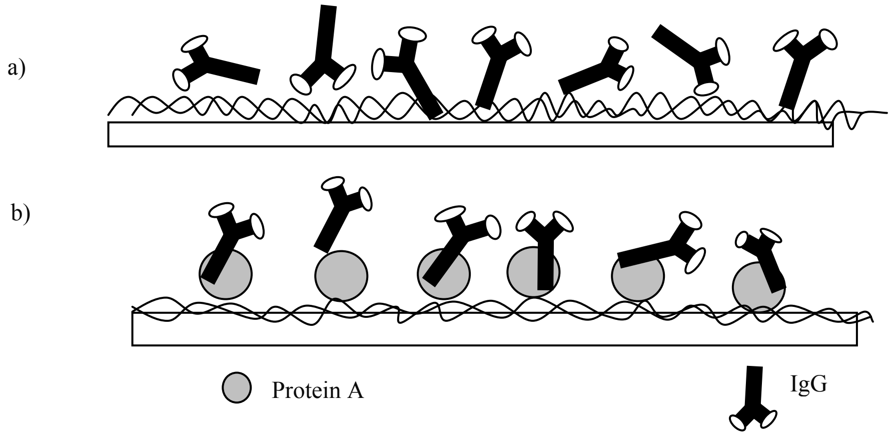

Figure 10. Schematic model of the spontaneous (a) and oriented (b) immobilization of IgG on the transducer surface of the immune biosensor. (a) IgG is immobilized on top of the PAA layer, (b) binding IgG with protein A deposited on top of the PAA layer.

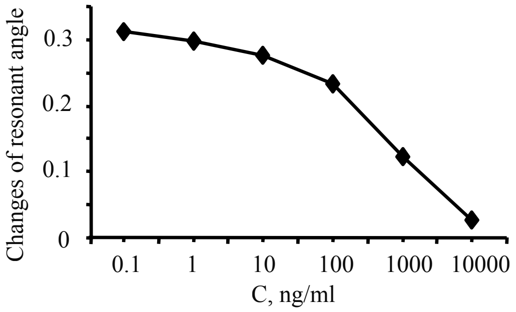

Figure 11. Response of SPR immune sensor vs. concentration of NphEO in analysed solution.

3.2. EIS-Based Biosensor

The general view of the EIS-based biosensor, the electronic part of which was developed at the Institute of Physics of Semiconductor of Ukrainian National Academy of Sciences, is presented in Fig. 12. The biosensor comprises two independent channels, each of which contains five measuring cells. The biosensor is operated by custom-made computer software.

Both channels of the biosensor contained nitrocellulose membranes with an immobilized conjugate of NphEO and protein. The immune analysis was conducted via competitive reaction, as immobilized NphEO conjugate and free NphEO in solution, which was to be analyzed, competed for specific antibodies. In the experiments, NphEO conjugated with ovalbumin was used. It was found that the sensitivity of the immune biosensors is about 10 ng/mL.

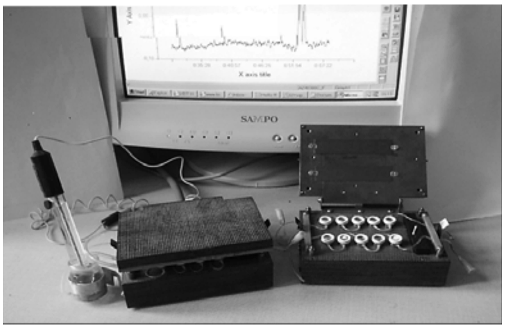

Figure 12. EIS-based biosensor.

3.3. ISFET-Based Biosensor

The ISFET-Based Biosensor is shown in Fig. 13. The recording part of this biosensor was made in the Institute of Biocybernetics and Biomedical Engineering of the Polish Academy of Sciences (Warsaw). The signal registration devices and two different types of chips are shown. Both of them contain two ISFETs: measuring and reference structures.

The data on sensitivity of immune biosensors based on ISFETs, EIS-structures and SPR are presented in Table 5. The sensitivity of ISFET-based biosensors is five times higher than the other ones. This suggests use of immune biosensors based on EIS-structure and SPR for water quality analysis at the initial and intermediate steps of water purification. At the same time, the use of immune sensors based on ISFETs is more preferable at the last step of water purification.

Figure 13. ISFET-based biosensor.

Table 5. Comparison of sensitivity of various immune biosensors during determination of NphEO in model solutions.

Immune biosensor	**Sensitivity, ng/mL**
ISFET-based	0.5-5
EIS-based	1-10
SPR-based	1-10

4. CONCLUSIONS

From the data presented above, it may be concluded that the biosensors developed provide effective measurement of toxicity at different stages of the process of water purification. During the water purification process, the following scenario of use of biosensors could be suggested. For control of total toxicity of initial water and for determination of individual toxic substances (for example of NphEO), it is necessary to use the bioluminescent test and one of the immune biosensors based either on EIS-structures or SPR. The thermal cell biosensors with *Sacchromices cerevisia* and *V. fischeri* are not effective at low concentrations of such toxic substances as detergents. The above holds for the intermediate step of water purification, i.e., after its treatment by ozone and UV-radiation. During the final step of water purification it is more suitable to use a *Daphnia magna* ChL biosensor or an immune biosensor based on ISFETs, as they are more sensitive in comparison with other immune biosensors.

ACKNOWLEDGMENTS

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RAPID DETECTION OF BACTERIA IN DRINKING WATER

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ABSTRACT

A heterotrophic plate count (HPC) is a measure of the total number of heterotrophic bacteria in a water sample. It does not indicate whether the bacteria are harmful or harmless to humans, but serves as an indicator of the cleanliness of the raw water and treatment processes. The most sensitive test uses the R2A agar and an incubation time of 7 days. Other media and shorter incubation times lead to lower counts. Whichever test is used, an incubation of 2-7 days makes the test clearly useless for operational decisions and intervention. Intentional or accidental contamination of a water supply must be determinable in minutes.

We have studied over the past three years several water sources, such as municipal water, bottled water, beach and pool water, and ballast water on ships. Using portable equipment, we have determined the ATP in the water sample by lysing the bacteria, adding luciferine/luciferase to develop light, and measuring the light emission in a luminometer. The test is not new and is described in Standard Methods. What is new is that the present test is more sensitive, the instrumentation fits on a clipboard, and the test can be done in the field at the location where the sample is taken. If the estimated HPC is high, a second step may be necessary to identify if there are pathogens in the water sample. A rapid test for *E.coli* O157:H7, *Pseudomonas*, and *Legionella pneumophila* has been developed using immunomagnetic separation. These tests take longer, but are still under an hour for each target bacterium. The detection of spores in the water sample is also possible. The essence of the method is that a contamination of bottled water with bacteria can be detected while the batch of bottled water is still on the shipping dock.

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INTRODUCTION

The current microbiological standards focus on a single group of indicator organisms for the bacteriological safety of drinking water (Federal Register 1996). Although the current standards of water quality have eliminated massive outbreaks of waterborne disease, a question has been raised about the adequacy of the standards of drinking water quality to prevent water-borne illnesses (Payment et al. 1991). Cases of gastrointestinal illnesses were reported among individuals drinking tap water that had met microbiological and physico-chemical water quality criteria. The determination of the total number of heterotrophic bacteria has been known as a better indicator of water quality than the coliform test because many opportunistic pathogens are not in the coliform group (Geldreich et al. 1972) and a high HPC has shown to interfere with the determination of the coliforms (LeChevallier et al. 1985).

The present HPC method using R2A agar is known to be the most sensitive test for enumerating bacteria from treated water (Reasoner et al. 1985). The disadvantage of the test is that it takes seven days to complete and when the results are known, the water has long been consumed. A test is needed that determines the total bacterial populations in a very short time so that corrective actions can be taken in a timely manner.

The ATP bioluminescence assay allows an estimation of bacterial populations within minutes and it can be applied on-site also. The estimation of the bacterial count based on the ATP of the water is not new. Standard Methods (APHA-AWWA-WEF 1995) indicate that the test requires one hour, one liter of water, and has a sensitivity of 100,000 cells. What is new is that our method is over 100 times more sensitive, requires one-hundredth of the sample volume, and is over 10 times faster. The test is also described and specified in (ASTM D 4012-81).

Thus the purpose of this study was to determine if a rapid ATP assay could estimate the bacterial populations in a practical and timely manner. For quality control purposes and to test the accuracy of both the ATP and HPC test, a direct enumeration of the bacteria in a water sample was done using two epifluorescence methods. One was the AODC method to enumerate the total number of bacteria, which include both the viable cells and the nonviable cells. The other was the DVC method that selectively enumerates viable bacteria.

MATERIALS AND METHODS

Water Samples

Water samples were obtained from drinking water fountains or distribution system sampling locations in the United States and abroad. The samples in the United States were taken from locations in California, Colorado, Florida, Georgia, Illinois, Kentucky, Maryland, Michigan, New York, Ohio, Oregon, Tennessee, Texas, Washington, and Washington, D.C. Some of the samples were obtained from airports (California, Illinois, Kentucky, Maryland, New York, Oregon, Tennessee, Texas, and Washington), and some were obtained from cooperating utilities (California, Colorado, Florida, Georgia, Michigan, and Ohio). A number of samples were obtained from Argentina, Australia, Austria, Brazil, Egypt, France, Germany, Hungary, Japan, Korea, Lithuania, Netherlands, Panama, Peru, Saudi Arabia, Switzerland, Ukraine, and the United Kingdom.

In August of 1999, a number of public drinking fountains were sampled in Paris, France. Samples were taken at the Charles deGaulle Airport, the Eiffel tower, Hospital Pitie, the Louvre, Notre Dame, Palais Chaillot, Sacre Coeur, and the UNESCO headquarters. The water samples were also analyzed for their metal content by ICP/MS.

Filtration of Samples

A Filtravette^{TM}, which is a combination of a filter and a cuvette with pore size of 0.45 microns, was placed into a Swinex filter holder (13mm, Millipore Corporation, Bedford, MA). A sterile syringe was used for drawing the water samples. The testing volumes of the water were between 0.1 and 10 mL, based on the expected number of bacteria in the sample. The filter holder was screwed onto the syringe and the water sample was pushed through the filter. The Filtravette^{TM} was taken out from the filter holder and placed onto a sterile blotting paper. The remaining water inside the filtravette was removed with a specially converted 3 ml syringe by applying gentle air pressure.

ATP Bioluminescence

A somatic cell releasing agent (New Horizons Diagnostic Corporation (NHD), Columbia, MD) was used to lyse all non-bacterial cells and release their ATP. Air pressure was used to remove the non-bacterial ATP through the filter. At this stage, the Filtravette^{TM} retains bacteria on its surface, and the bacterial ATP remained within the bacterial cell membranes through this step of the procedure. The Filtravette^{TM} was inserted into the microluminometer (Model 3550, NHD, Columbia, MD) (Fig. 1) and the bacterial cell-releasing agent was then added to lyse the bacterial cells retained on the surface of the filter. The released bacterial ATP was mixed with 50 µL of luciferin-luciferase (NHD, Columbia, MD) and the drawer of the microluminometer was closed. The light emission was recorded after 10-second integration of the light impulses and the unit was relative light unit (RLU). The result was expressed as RLU/ml by dividing the RLU values by the filtered water volume. The detection limit and sensitivity of the luminometer was tested with serially diluted ATP solutions (NHD, Columbia, MD). Distilled deionized water was used for the dilution and the pH was 7.8. The activity of the luciferin-luciferase was checked by using an ATP standard (NHD, Columbia, MD). The RLUs are proportional to the amount of ATP, and the amount of ATP is proportional to the number of viable bacteria.

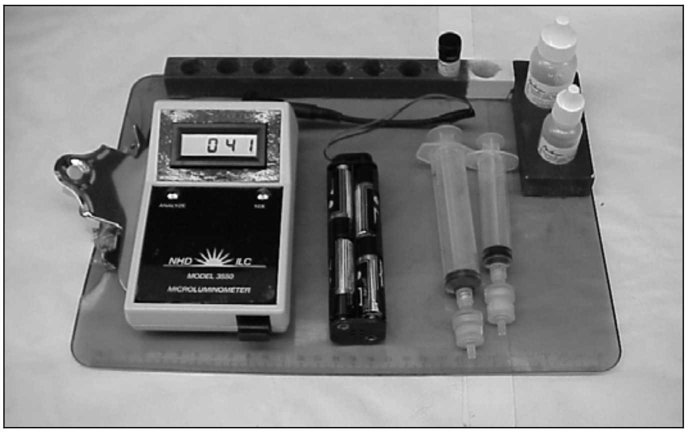

Figure 1. Portable microluminometer with accessories.

Bacterial Enumeration: AODC, DVC, HPC

The total (nonviable and viable) bacterial cells were determined from formaldehyde fixed (2%, v/v, final concentration) samples with the AODC method (Hobbie et al. 1977). The bacterial cells were stained with acridine orange (0.01%, w/v, Fluka, Switzerland) after filtration onto a 0.2 micron pore-size black polycarbonate membrane filters (Poretics, Livermore, CA). Cells were enumerated at a magnification of x1000 with an Olympus Provis epifluorescence microscope (Olympus Optical Co., Japan) equipped with a mercury arc lamp and a 460 - 490 nm excitation filter. The number of bacteria was counted in 10 microscopic fields using three subsamples and was then averaged. The number of bacteria per milliliter of sample was calculated using the equation in Standard Methods (APHA-AWWA-WEF, 1995).

The viable cells were counted by the DVC method (Coallier et al. 1994) with some modifications. The samples were incubated with yeast extract (0.005%, w/v, Difco, Detroit, MI) and nalidixic acid (10mg/L, Sigma, St. Louis, MO) without dilution for 24 hours at 20^{o}C. The modifications were: use of a lower concentration of yeast extract and no dilution. After incubation, the fixation, counting, and calculation of elongated bacteria were done following the AODC method.

The HPC was determined for each water sample in triplicate using R2A medium (Difco, Detroit, Michigan). The bacterial colonies were counted after an incubation period of 7 days at 28^{o}C.

RESULTS AND DISCUSSION

The detection limit of ATP was determined with high accuracy (r=0.999). It showed that the microluminometer was able to determine ATP concentrations as low as 0.2 picogram. It is known that the average ATP content in one bacterial cell is about 10^{-15} g (i.e., 1 femtogram) (Crombrugge et al. 1991). Thus the 0.2 picograms correspond to 200 bacterial cells.

About 120 water samples were analyzed with ATP bioluminescence, HPC, DVC and AODC methods, each in triplicate. A statistical analysis of the data shows that there are high correlation coefficients between ATP, HPC, DVC, and AODC, The correlation coefficient between ATP and HPC was 0.84, and the correlation coefficient between ATP and DVC was 0.8. Both are statistically highly significant. The prediction of the HPC can be accomplished by the following equation: HPC (CFU/mL) = $\text{RLU}^{1.47}$

The Paris drinking water samples were analyzed using 3 methods: The ATP assay, the HPC using R2A agar, and the plate count according to French standards (Casein peptone 5 g, Yeast extract 2.5 g, Glucose 1 g, agar 15 g/L of distilled water; incubate at 22°C for 3 days). Since the water samples were in transit for about two days one should not place great emphasis on the absolute numbers, but rather the relative relations. The R2A counts were about 30 times higher than the counts obtained by using the French method. The water quality varied significantly from location to location, and the visual observation of the plates showed quite different colonies in size and color. Subsequent analysis of the water for its metal content showed that the water had come from quite different sources. The metal concentrations are shown in Table 1, and the bacterial concentrations are shown in Table 2.

A recently published paper (Delahaye 2003) confirms the wide variations in the drinking water quality due to its many different sources. It also shows that the French (and European) methods grossly underestimate the bacterial counts.

Table 1. Concentrations of metals (µg/L)

Location	**Pb**	**Li**	**Mg**	**Sr**	**Ba**	**Al**
Palais Chaillot	0.2	0.8	2,659	142	14	1.1
Eiffel Tower	3.1	1.2	1,454	135	24	1.5
Hotel St Andre	5.0	1.5	1,421	125	28	1.2
Notre Dame	3.6	1.0	1,365	128	30	1.2
Parc Viviani	91	1.5	1,665	135	31	2.6
Near Louvre	2.4	1.4	1,647	133	29	1.9
Hospital Pitie	0.6	2	2,400	225	26	13
UNESCO	5.5	1.2	1,930	151	26	1.2
Sacre Coeur	0.3	2.1	4,570	397	23	6.0
CDG Airport	0.02	2	5,370	463	17	20
Bottled Water	0.02	12	16,000	1,100	19	0.7
H_2O Dispenser	0.1	0.7	4,781	224	27	0.8

Table 2. Bacteria in Paris drinking water (No/mL).

Location	**RLU***	**HPC****	**FM*****
Palais Chaillot	728	1735	250
Eiffel Tower	435	10,920	2,300
Hotel St Andre	952	45,000	18,220
Notre Dame	4	65	10
Parc Viviani	296	16,310	1,000
Near Louvre	10	80	15
Hospital Pitie	539	52,000	3,610
UNESCO	47,600	1760,000	2,000
Sacre Coeur	27	33	5
CDG Airport	173	4,670	170
Bottled Water	13	108	2
H_2O Dispenser	813	57,400	4,350

*RLU = relative light units, **HPC = heterotrophic plate count, ***FM = French method.

CONCLUSIONS

This is the first study where a miniaturized ATP bioluminescence method has been validated against the conventional plate method, the direct viable count, and the acridine orange direct count for the determination of heterotrophic bacteria in the drinking water samples. The ATP assay was found to be rapid and sensitive. The procedure is simple and can be done on-site with a portable power supply. The volume of water needed for filtration is small (0.1-10 mL). A traveler wishing to determine the bacterial water quality in a foreign country will be able to do this in minutes.

FURTHER STUDIES

In water with a high HPC, it is advisable to look for pathogens. Specific bacteria can be isolated from the water using immunomagnetic separation (IMS). Studies have been done to estimate the number of *E.coli* O157:H7*, Pseudomonas* and *Legionella.* After separation, the target cells are lysed and their number is estimated. This has been reported in a recent paper (Lee, 2001).

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UTILIZATION OF MOBILE ANALYTICAL TESTS IN WASTEWATER TREATMENT PLANT

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ABSTRACT

This paper deals with the choice of detector for organic pollution in wastewater. The AOX detector is characterized and explained in detail. These mobile analytical measuring tube systems were used during the inspection of wastewater treatment plants in a particular region and the results are compared with methodology based on microcalorimetry.

INTRODUCTION

Wastewaters are one of many sources of environmental pollution. The composition of municipal wastewaters is determined by the composition of their individual components and the correlation of their volume proportions. The composition of these parts and their correlation is not always the same and that is why there is a considerable variability in the composition of municipal wastewater. The concentration of some substances is considerably increased due to the industrial pollution; on the other hand ballast waters can sometimes significantly reduce the concentration of harmful substances in municipal wastewaters. As the measures for controlling wastewater discharge from municipal and industrial sources of pollution are tightened up and at the same time the number of monitored parameters is increased this places higher demands on the methods of analyses being used.

The advantage of the standard methods being used for wastewater discharge control is their high sensitivity, accuracy and reliability; however they are not able to provide information in a short time period. That is why non-standard analytical procedures are necessary for water quality control at the inlet and outlet from the wastewater treatment plant. These analytical

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procedures are so called mobile screening methods with fast applicability, easy operation and a high level of data reliability.

THEORETICAL PART

Municipal wastewater pollution is assessed with respect to the sewage regulations, the government regulations concerning the allowable water pollution and the Act on charges for wastewater discharge into surface waters. The main indicators of pollution are as follows: COD_{Cr}, BOD_5, undissolved substances, dissolved inorganic substances, ammonium ions ($N\text{-}NH_4^+$), inorganic nitrogen ($N_{inorg.}$) and total phosphorus (P_{total}). Indicators of organic pollution are biochemical oxygen demand BOD_5 or chemical oxygen demand COD_{Cr}, total organic carbon (TOC).

The halogen-containing organic contaminants belong to highly monitored substances during the analysis of the environmental samples and they can be classified by the procedure employed for their separation as follows: TOX (total organic halogens); DOX (dissolved organic halogens); AOX (adsorbable organic halogens) – on activated charcoal; EOX (extractable organic halogens) – by hexane; POX (purgeable organic halogens) – can be released from water at 60 °C; VOX (volatile organic halogens) – can be released from water at 95°C and adsorbed on tenax; and TX (total halogens) organically and inorganically fixed halogens.

AOX is an important parameter for water quality assessment. It contains the total content of organically fixed chlorine and bromine, which can be adsorbed on activated charcoal. The value of AOX can cover both volatile halogenated hydrocarbons (mainly chlorinated solvents and cleaning agents), and less volatile compounds such as PCBs, chlorinated benzofurans, polychlorinated paraffins (hydraulic and transformer oils). The AOX value is significantly affected by the products of chlorination of natural high-molecular organic substances such as polysaccharides, humic acids, lignin, etc.

This type of compound is characterized by higher toxicity and difficult biological degradability when compared to other organic substances. With respect to supplying inhabitants, the compounds have dangerous properties such as bioaccumulation, toxicity, mutagenicity and carcinogenicity. They easily accumulate in adipose tissues of organisms due to their lipophilic character.

The concentration of AOX substances is as follows: (i) usually lower than 5 μg/L in drinking water of underground origin, (II) up to 10 μg/L in drinking water of surface origin, (iii) about 3 μg/L in clean surface waters, (iv) up to 1 mg/L in waters polluted by industry, (v) 20–370 μg/L in municipal waste waters (Pitter 1999).

Summary assessment of AOX in the Czech Republic is carried out by Labtech Brno according to the EN 1485 standard with the help of an LTX-2000 analyzer, which operates on the principle of oxidative microcalorimetry, i.e. organic halogenated substances are burned for five minutes in an oxygen stream at a temperature of 950°C. The halogen hydrides produced are then assessed by computer aided automatic microcoulometric titrimetry. Calibration of the device is usually carried out using chlorophenol. AOX and TX can be assessed by the basic version of the LTX-2000 and EOX and POX with argon as carrier gas (99.996 % purity) can be assessed with additional modules.

Many firms were forced to develop fast assessment methods for these substances due to the demand for fast and high-quality results. At present there are a number of products to determine AOX photometrically after prior thermal decomposition. Most products are based on measuring tube systems produced by Macherey-Nagel, or Merck from Germany (Macherey-Nagel 2000). These measuring tube systems were used during the inspection of the wastewater treatment plants in particular regions and the results were compared with methods based on microcalorimetry.

The monitored wastewater treatment plant No. 1 in the town of Prostějov, Czech Republic was built as an activation mechanical-biological wastewater treatment plant with sludge fields and mud-setting pits. The wastewater treatment plant No. 2 in Vyškov, Czech Republic was designed and implemented as a mechanical-biological plant with removal of nutrients, anaerobic stabilization of sludge by mesophilic digestion and removal of sludge water on a centrifuge.

EXPERIMENTAL PART

The following devices were used in the experimental part of the work: Nanocolor® 400 D (Macherey–Nagel) system photometer (wavelength 470 nm) and TR-200 (Merck) thermoreactor, see Figure 1.

The following measuring tube systems were also used: AOX set for the preparation of samples including 200 ml of rinsing concentrate for AOX R1, a tube with Nanofix® R2 capsules, 105 ml of AOX R3 agent (2% sodium hydroxide), 75 mL of AOX R4 agent, 20 reaction glasses 14 mm ID, 20 test tubes AOX (nitric acid), 2 test tubes Chloride R2 (mercury thiocyanate), Chromafil® CA-45/25 S diaphragm filters, and other laboratory glassware and tools.

Wastewater treatment plant sampling was carried out at the inlet and outlet, in compliance with the EN 25667 standard. Sampling for AOX was carried out regularly; 12 times per month during one quarter and the analysis (with the help of tests and analyzers) was carried out on the same day.

Figure 1. Photometer Nanocolor® 400 D and Thermoreactor TR-200.

Table 1. Used Nanocolor® measuring tube tests.

Parameter	Measurement range, mg/L	Test No.
AOX	0.10 – 3.00	0071
AOX	0.01 – 0.30	0072

The AOX assessment from the aqueous sample was carried out in three steps:

1. Solid phase extraction with Nanosorb® for AOX;
2. Decomposition of the concentrated adsorber medium;
3. Determination as chloride with the reagent set Nanocolor® AOX 3.

The AOX assessment according to the EN 1485 standard was carried out in three steps:

1. Homogenization;
2. Adsorption (by shaking or on a column);
3. Combustion (LTX-2000 analyzer) and microcoulometric argentometric titration (CSN EN 1996, Maly and Mala 1996).

RESULTS AND DISCUSSION

The AOX values, which were assessed with measuring tube tests, were about 0.11 mg/L at the inlet to the wastewater treatment plant No. 1 during the monitored time period (February-April 2003). Similar concentrations were detected at the outlet as well. The Czech Republic concentration limit of 0.20 mg/L for applying charges was exceeded once (0.25 mg/L) at the cleaned water outlet during the time period monitored as is apparent from Fig 2.

There were more significant differences in the measured AOX in wastewater treatment plant (Macherey-Nagel 2000). The minimum concentration at the outlet was 0.06 mg/L and the maximum concentration was 0.30 mg/L. It was found that the AOX values measured at the outlet of monitored wastewater treatment plant No. 2, are long-term lower at 0.12 mg/L, whereas it is 0.14 mg/L in wastewater treatment plant No. 1.

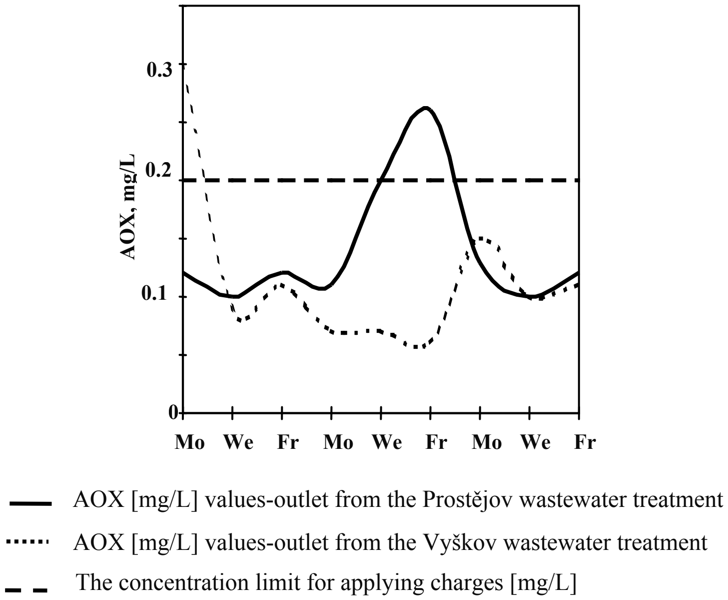

Figure 2. Changes of AOX values at the outlet of two monitored wastewater treatment plant during three weeks.

The results obtained using tube tests were compared with the results obtained using the LTX-2000 analyzer operating according to the EN 1485 standards. No significant differences were found, as is apparent from Tables 2 and 3.

Simultaneously with the inlet/outlet wastewaters pollution monitoring the impact of standing time after sampling on the reliability of assessment was analyzed. Changes within 5 days are shown in Figure 3.

Table 2. Comparison of the AOX values measured with the help of LTX-2000 analyzer and tube tests (No. 1).

Method of assessment	February	March	April
AOX inlet/outlet according to EN 1485, mg/L	0.158/0.124	0.130/0.126	0.141/0.115
AOX inlet/outlet tube tests, mg/L	0.16/0.12	0.13/0.13	0.14/0.11

Table 3. Comparison of the AOX values measured with the help of the LTX-2000 analyzer and tube tests (No. 2).

Method of assessment	February	March	April
AOX inlet/outlet according to EN 1485, mg/L	0.175/0.135	0.167/0.164	0.148/0.125
AOX inlet/outlet tube tests, mg/L	0.17/0.14	0.17/0.16	0.14/0.13

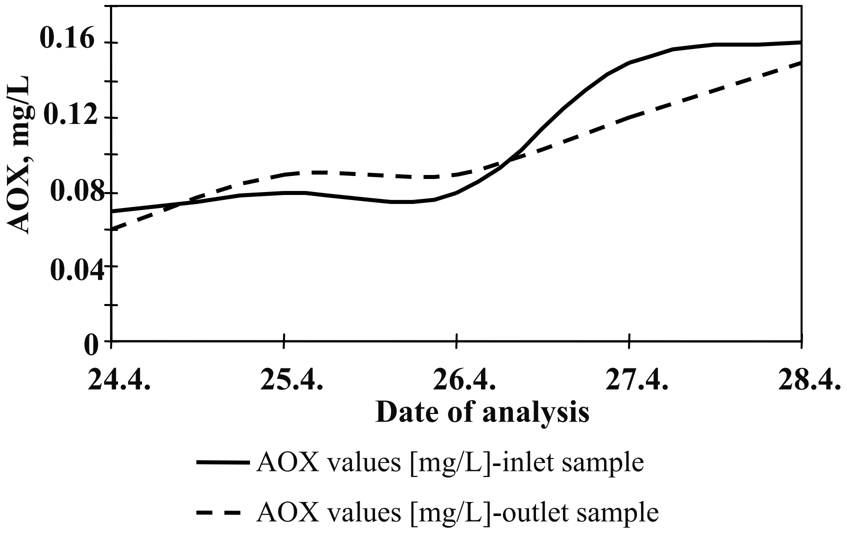

Figure 3. Changes of the AOX values in the wastewater sample during 5 days.

It is clear that the AOX values are not significantly influenced during the first three days. After that the AOX values increase by ca 100% and the results do not correspond to the real content of substances in the sample. This can be explained by the change of chemical equilibrium in the water sample, where certain inorganic chlorides gradually bond to organic substances.

Table 4. Time of analysis vs. price of analysis carried out by analyzer and tube tests.

Analysis phase tube test	Duration [min]/ Price [€]	Analysis phase LTX analyzer	Duration [min]/ Price [€]
Extraction with Nanosorb® column	ca. 10 - 15	Preparation of samples and reagents	ca. 25 – 30
Decomposition of concentrated medium	ca. 30	Shaking	60 (EN 1485)
Cooling	ca. 10 - 15	Reference sample	ca. 25 – 30
Filtration	ca. 3 – 4	Filtration Combustion	ca. 10 – 15 ca. 5
Assessment	ca. 3 (reaction time)	Assessment	ca. 10
Total duration of analysis	ca. 60	Total duration of analysis	ca. 150
Price	27	Price	76

This results in the creation of difficult to destroy complexes and a positive increase of the AOX values in the samples being stored for more than 3 days. Similar findings are noted in (Neupert 1986, Macherey-Nagel 2000).

The use of tube tests for the determination of organic halogenated substances in wastewaters is not only less time demanding but also significantly cheaper in comparison with the analyzer method. This is presented in Table 4.

CONCLUSIONS

This paper described water quality control at selected wastewater treatment plants. Both treatment plants monitored are mechanical-biological, where the biological treatment is carried out with the help of activated sludge.

The AOX content was monitored with the help of tube tests, which were part of more detailed water quality control measures. The AOX content is monitored with respect to the concentration limit for applying charges set by law and it only once exceeded the limit of 0.20 mg/L at both wastewater treatment plants monitored. The values of AOX at the inlet and outlet of both wastewater treatment plants monitored did not differ very much. This results from the above-mentioned information that there is hardly any removal of AOX pollutants at the wastewater treatment plants.

The work is beneficial for comparing the methods being used for the assessment of AOX organic pollution. Mobile tube tests were compared with a standard method used in accredited laboratories and wastewater treatment plant laboratories. Comparability of both methods was proved with respect to both the measurement range and the accuracy of data collected. It was proved that the application of mobile tube tests has many advantages. These tests are: (i) time and physically undemanding, (ii) operated by a semi-skilled worker if need be, (iii) do not require many chemicals or special laboratory equipment, and (iv) economically advantageous.

It is assumed that the strong pressure by state authorities to raise the quality of discharged waste waters, as well as the number of regional, national and international activities focused on the analysis of water will result in the introduction of these mobile monitoring methods into routine laboratory practice.

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AN EVALUATION OF THE EFFICACY OF THE MIXED-OXIDANT SOLUTIONS PRODUCED FROM "ACTIVATED WATER" IN COOLING TOWER BIOLOGICAL CONTROL

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ABSTRACT

The main objective of this study was to further enhance the environmental protection by lowering the extend of environmentally harmful water treatment. Therefore, a comprehensive trial evaluation of the efficacy of the mixed-oxidant solutions produced from "activated water" in cooling tower biological control was conducted on two Midlands-based industrial sites.

Activated water (ECAL) is an electrochemically generated mixed-oxidant solution (MIOX). The ECAL replaced conventional oxidising biocides (chlorine and bromine) for cooling tower microbiological maintenance. A comprehensive sampling protocol was employed to evaluate the efficacy of activated water, against *Legionellae* and heterotrophic bacteria in four cooling towers, which were chosen as the most challenging applications. All of the cooling towers remained free from *Legionellae* throughout a twelve month evaluation period, despite the previously demonstrated presence of *Legionellae* in all four of the towers studied at levels well in excess of UK Health and Safety Commission (HSC) Approved Code of Practice and Guidance (ACOP) upper action limits. Levels of heterotrophic bacteria were controlled below Cadbury Trebor Bassett's (CTB's) and TIMET UK Ltd's own limits of 10^5 cfu/ml in all towers and below 10^4 CFU/ml throughout the evaluation.

The results proved direct evidence of significant activity against biofilm bacteria, with biofilm removal beginning almost immediately after commissioning of the mixed oxidant treatment programme. The results

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obtained were significant and illustrated the following potential benefits for CTB and TIMET*:* (i) aggressive disinfection-elimination of biofilms, (ii) inactivation of pathogenic organisms including *Legionella* species, and nil or low aerobic bacterial counts, all without additional biocides; (iii) safe operation because only salt, water and power are used to generate the non-hazardous, mixed oxidant solution; (iv) liability exposure and associated management costs are reduced; (v) staff and community safety is improved, and costs for safe transportation, handling and storage of hypochlorite, chlorine dioxide or bromine are eliminated; (v) low maintenance-automated system requires only minimal operator attendance; (vi) cost competitive-low operating costs and no safety costs usually result in a lower lifecycle cost; (vii) potential to introduce technology to many other areas that are currently using consumable disinfection or CIP (*c*leaning *i*n *p*lace) products with resultant cost and environmental impacts.

INTRODUCTION

The major challenges in cooling tower maintenance include: (1) controlling deposition on cooling surfaces ($CaCO_3$, $CaSO_4$ and SiO_2 deposits); (2) providing corrosion protection for copper, copper/nickel tubing, admiralty (copper alloy) and carbon and stainless steels; (3) controlling microbiological growth including biofilms on cooling surfaces and bacterial counts in the cooling tower bulk water including *Legionellae*; (4) controlling airborn impurities, contaminants and particulates washed out of the air and other contaminants that enter via the incoming water supply and external to the water source.

These challenges can be addressed and at least partially controlled by additions of various antisealants, corrosion inhibitors, and biocides, plus use of a disinfectant continuously supplied to provide a residual disinfectant level. Chlorine and bromine are currently the preferred disinfectants, due to their relatively low cost, ease of use and control and their ability to maintain a disinfectant residual. However the use of biocides is being viewed with increasing concern by the regulatory agencies from the standpoints of safe transportation, storage and handling and the residues of the biocides in the cooling tower blow down. Thus, there is a need in the cooling tower maintenance industry for a disinfection system that will provide enhanced cooling water disinfection, allowing the elimination of biocide use, whilst maintaining simplicity, reliability, and ease of operation and causing minimal corrosion and scaling impact on the heat exchange and cooling surfaces of the cooling system.

Mixed oxidant generators have been manufactured and marketed since 1994 following a period of intense development and testing. The systems were primarily designed for the medical market (endoscope sterilisation) and the agricultural markets, but have now achieved success in applications in; cooling towers, L8 domestic services, food preparation, CIP, swimming pools, water features, and extensive *Legionellae* control. MIOX systems use an electrolytic process to generate mixed oxidants in solution on-site and on demand, this is achieved by electrolysing a weak brine solution, so there is no need to transport or handle hazardous materials. In addition, the mixed oxidant produced is dilute and is not hazardous to employees.

The mixed oxidant solution consists primarily of chlorine (as HOCl and OCl^- depending on pH), as well as other chlorooxy species, which are short-lived when present with an oxidant-demanding substance, i.e. they react and are no longer detectable in water, leaving the chlorine component as the measurable residual. The relative disinfecting capabilities of the MIOX, which are significantly greater than those of chlorine alone, are believed to be caused by the synergism of oxidants working together. MIOX solutions have extremely low toxicity along with well-documented broad-spectrum biocidal activity (Tapper 1997, Tsai et al. 1998, Shetty et al. 1999). Zinkevich et al. (2000) reported that the mode of action involves the destruction of chromosomal and plasmid DNA, RNA and proteins.

Residence of *Legionellae* within biofilms is a particular problem in cooling tower systems (HSC 2001), and it can prove difficult to eradicate by conventional means. LeChevalier et al. (1988) reported that biofilm can be up to 3,000 times more resistant to standard chlorine disinfectants than unattached cells, but Bradford and Baker (1995) and Crayton et al. (1997) have demonstrated that mixed oxidants, in contrast, exert dramatic activity against biofilms. MIOX solutions have a history of almost three years usage in cooling tower treatment, and highly satisfactory results have been obtained to date using HSC ACOP monitoring protocols with continuous negative *Legionellae* tests results. MIOX solutions show rapid biocidal efficacy against *Legionellae* in the EN 13623 standard suspension test.

Mixed-oxidant solutions have been shown to provide the disinfection needed to meet or exceed all bacterial/residual standards in potable water and to exceed all other current chlorine based technologies in kill effectiveness of viruses and oocysts whilst also reducing disinfection by-product concentrations compared to chlorine. For example, the mixed oxidant solution can inactivate more than 99.9% of *Giardia lamba* cysts and *Cryposporidium parvum* oocysts at practical doses (as free available chlorine, FAC) of 5 mg/L; in the case of *C. parvum* oocysts no inactivation occurs by equal doses of chlorine alone.

The disinfection ability of the MIOX solution, in contrast to chlorine, has also been studied in simulated cooling water with three bacteria species relevant to the cooling industry: *Bacillus sternotherus, Pseudomonas aeruginosa,* and *Legionella pneumophila.* The results of these tests at pH 8 after 10 min exposure are shown in Table 1. Mixed oxidants were significantly more effective than chlorine at achieving total inactivation of all bacteria, even at doses as low as 2mg/L FAC.

Table 1. Mixed oxidant performance compared to equivalent levels of chlorine.

Type of microorganism	Initial microorganism concentration, CFU/mL	Final microorganism concentration (CFU/mL) at two different chlorine equivalent concentrations of MIOX and hypochlorite			
		2 mg/L		4 mg/L	
		Mixed Oxidants	NaOCl	Mixed Oxidants	NaOCl
Bacillus stearothermophilus	2 x 10^5	35	1400	0	12
Pseudomonas aeruginosa	1 x 10^5	0	1200	0	110
Legionella pneumophila	1 x 10^5	0	> 2	0	> 2

HSC action limits for cooling towers define total viable counts (TVCs) of less than 10^4/mL and *Legionellae* of less than 100/L as indicators that a cooling system is under microbial control. TVCs between 10^4 and 10^5/mL and/or *Legionellae* counts up to 10^3 require a review of control measures and TVCs greater than 10^5 and/or *Legionellae* counts in excess of 10^3/L require immediate corrective action. HSC also states that oxidant levels should not be allowed to consistently exceed 2 ppm in order to avoid corrosion problems, though levels in excess of this are permitted in exceptional circumstances. HSC recommendations for microbial monitoring specify weekly analysis of single samples for TVC in cooling water by dip slide, with make-up water monitored quarterly, together with quarterly analysis of a single sample of cooling water for *Legionellae*, using a United Kingdom Accreditation Service (UKAS) accredited laboratory (HSC 2001)

The above parameters were therefore used as benchmarks in the study, except that this study significantly increased the scope and frequency of microbial analysis. Bentham (2000) reports that the variability of *Legionellae* counts in cooling tower systems is so high that risk assessments cannot be reliably founded on single or infrequent analyses. *Legionellae* concentrations in cooling tower systems may vary by as much as 3 orders of magnitude within 10 minutes (Bentham and Broadbent 1993). Furthermore, although weekly TVC analyses of cooling water are specified by the HSE as a means of assessing microbial control, a number of studies have shown that there is no evidence of any correlation between TVC and the presence of *Legionellae* in cooling tower systems (Liu et al. 1993, Pinna 1996).

Sampling for both TVC and *Legionellae* was therefore carried out on all towers on a twice weekly basis, with duplicate sampling for each taken 10 minutes apart to provide an indication of variability within the systems. TVCs were conducted using laboratory base plate methodology and thiosulphate inactivation was employed in order to facilitate a proactive and comprehensive evaluation. In addition, TVCs were also monitored by dip slides as in normal commercial practice.

MATERIALS AND METHODS

Test Site and Towers. Trial site 1

All of the cooling towers were located at CTB's main manufacturing plant at Bournville, Birmingham. Prior to this study using activated water, all towers had been treated with bromine, supplied as bromo-dichlorohydantoin, at levels typically in the range 1.0 to 2.5 ppm, with periodic episodes where dosing was required at 3 to 5 ppm.

Towers Nos. 32, 33, 93, and 12 used in this evaluation were chosen because they were in excess of twelve years old with varying degrees of corrosion present. Due to the nature and positioning of these towers pressure jet washing is not permissible. All towers demonstrated heavy use over many years and therefore represented the biggest challenge for any treatment process.

Tower No. 32, serving refrigeration plant, is a film cooling tower having some wooden internal structure, induced twin cell tower, mild steel sump, metal exterior cladding, wooden top fan housing, and plastic packing. Evidence of biofilms and severe corrosion is present. The maximum system capacity is 5 m^3. Tower No. 93 is a BAC spray induced cooling tower with maximum system capacity of 2.5 m^3. Tower No. 33 is a film cooling fibreglass tower with plastic fill pack and eliminator; maximum capacity 0.5 m^3. Installation No. 12 comprises a pair of film cooling fibreglass towers having plastic fill and eliminator, maximum capacity 4 m^3. Towers Nos. 32, 33, and 93 were supplied with town mains make-up water. Twin Towers No. 12 were supplied with filtered and chlorinated river water make-up.

Towers Nos. 32, 33, 93, and 12 were treated using a mixed oxidant generator (Fig. 1), with the dosage controlled via an in-line Sentek redox

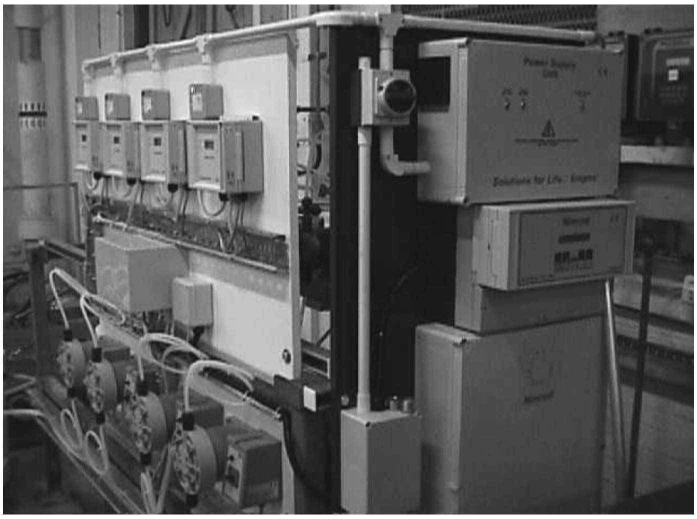

Figure 1. Mixed oxidant generator supplying activated water to the cooling towers.

control system. A specific organic inhibitor programme designed by Waterman Environmental Services Ltd for yellow metal and steel corrosion inhibition was used throughout this evaluation. No other biocides were used. Pre-study monitoring of the towers was commenced 58 days prior to commissioning of the mixed oxidant programme, when all of the systems were utilising bromine treatment.

Test Site and Towers. Trial site 2

All the cooling towers, including the TIMET main tower and RA 220, were located at TIMET's main manufacturing plant at Aston, Birmingham. Prior to this study, using ECAL mixed oxidant solutions, all towers had been treated with bromine, supplied as bromo-dichlorohydantoin, or sodium hypochlorite at levels typically in the range 0.5 to 1.5 ppm. All towers were supplied with town mains make-up water. The towers were treated using a mixed oxidant generator, with the dosage controlled via an in-line Sentek redox control system. A specific organic inhibitor programme designed by Waterman Environmental Services Ltd for yellow metal and steel corrosion inhibition was used throughout this evaluation. No other biocides were used. Pre-study monitoring of the towers was commenced 180 days prior to commissioning of the mixed oxidant programme, when all of the systems were utilising bromine or chlorine based treatment.

MICROBIOLOGICAL AND CHEMICAL ANALYSES

The towers were sampled twice weekly by taking 1 L volumes from the tower sumps into sterile vessels containing a sufficient amount of sodium thiosulphate to bring the final concentration to 1% v/v. Separate 1 litre samples were taken for *Legionellae* and TVC analyses, and this sampling procedure was repeated after 10 min, providing duplicate samples for both *Legionellae* and TVC analysis. The samples were maintained at 4°C for TVC and 4-18°C for *Legionellae* in transit to the laboratory and delivered there on the day of collection. All microbiological analyses were performed by a UKAS (NAMAS) accredited laboratory participating in the Public Heath Laboratory Service Water Microbiology External Quality Assessment Scheme. Analyses of *Legionellae* were performed using the membrane filtration method with a lower detection limit of 100 CFU/L. Heterotrophic TVC analyses were performed using yeast extract agar pour plates and appropriately diluted samples, incubated at 30°C for 3 days. Samples of cooling and make-up water were collected weekly for full chemical analysis. Oxidant reserves were recorded during each sampling by the DPD method.

Dip Slide Methodology

Dip slide samples were taken twice weekly from all four cooling tower sumps following the manufactures instructions. All dip slides were incubated for 48 hours at 30°C.

Biofilm Monitoring Methodology

All towers were fitted with stainless steel biofilm coupons; these were positioned in low flow areas of the tower sumps at three different heights, near the base, mid water and at the surface film. Analyses of biofilm coupons for TVC and *Legionella pnuemophilia* detection were conducted at 91 days and 180 days using the method followed and described in full in the ISO (1998).

Corrosion Monitoring Methodology

Corrosion coupons were placed in serpentines with monitored flow rates at each cooling tower; the metals tested were mild steel, copper, and stainless steel. Measurements by corrator probes were also undertaken.

RESULTS

Trial Site 1

Legionella pneumophila sero-groups 2-14 were isolated from Tower No. 32 at a level of 1900CFU/L and from Tower No. 93 at a level of 4000 CFU/L, two weeks prior to the start of the pre-study evaluation, during the course of routine ACOP monitoring whilst the towers were still under bromine treatment. Treatment and sampling regimes were modified immediately as required by Cadbury Trebor Bassett internal procedures; all within the requirements laid out under the Approved Code of Practice L8. Notably, no *Legionellae* were detected from any activated water treated tower during the twelve months of this evaluation.

No *Legionellae* species were isolated from any coupon throughout this trial. The level of TVCs recorded from coupons was either nil or of insignificant numbers to constitute a biofilm. These results represent a 99% reduction from previously observed biofilm formation. This fact will not only assist with *Legionellae* suppression, but also will reduce or eradicate significant energy losses from *Pseudomonas* colonisation.

All measured corrosion rates were well within current industry norms for mild steel, stainless steel and copper. All measured corrosion rates were reduced from previous levels. The actual corrosion reduction levels when compared to previous historical data represent significant improvements. Improved corrosion rates will not only assist with *Legionellae* suppression but will serve to extend the useful life cycle of towers of this type. Corrosion control featured Waterman's patented programme of combined inhibitors for mixed oxidant dosage.

Trial Site 2

Legionella pneumophila sero-groups 2-14 were isolated from the main tower on five separate occasions at levels of 50, 500, 1300, 100, and 1200 CFU/L prior to the mixed oxidant dosage trials. From the new RA 220, *Legionella pneumophila* sero-groups 2-14 were isolated on four separate occasions at levels of 50, 80, 400, and 240 CFU/L during the course of routine ACOP monitoring prior to activated water dosage whilst the towers were still under bromine treatment. No *Legionella* were detected from any mixed oxidant treated tower during the 12 months of this evaluation. Biofilm data and reduction of corrosion rates were similar to those obtained for trial site 1.

DISCUSSION

Most studies of microbial control measures in cooling tower systems employ a minimalist sampling protocol, usually based on HSC ACOP recommendations for routine surveillance of microbial quality in cooling systems, which according to Bentham (2000) is unlikely to produce findings of much significant value. The sampling regime used in this study, by contrast, provides comprehensive replicate data, which facilitates far more meaningful conclusions than would normally be the case. Given the nature of the sampling regime employed, the absence of *Legionellae* from any of the towers following the commissioning of the mixed oxidant system is a significant finding, particularly so when towers Nos. 32 and 93, the TIMET main tower and RA 220 provided evidence of *Legionellae* colonisation in the pre-study period.

The TVC results showed a consistent pattern of high counts and high variability immediately after commissioning followed by a decline to base levels with sporadic individual higher counts. This is consistent with biofilm removal as a consequence of activated water commissioning, supporting the contention of other investigators (Bradford and Baker 1995, Crayton et al. 1997) that mixed oxidant solutions are more effective than conventional single oxidising species. The results obtained in all tower systems were extremely good, but mention should be made specifically of towers Ta and more importantly tower Td. Tower Ta, whose pack could not be removed, generally demonstrating poor internal conditions, was effectively cleaned of all biofilm on line; this existing biofilm which was present under a continuous brominating programme was the probable source of the *Legionellae* contamination. The bacteria control with very small oxidant reserves (0.5-1.0 ppm) witnessed in tower Td was remarkable when the make-up water quality both in terms of organic load and biological content is considered. This make-up supply provided a constant and significant biological challenge that the activated water met with some ease.

The TIMET trial results obtained in all tower systems were extremely good, but mention should be made specifically of RA220 and more importantly the main tower. Tower RA220 was effectively cleaned of all biofilm on line; this biofilm was also present under a continuous brominating programme and was the probable source of the *Legionellae* contamination. The bacteria control with very small oxidant reserves (0.5-1.0 ppm) witnessed in the main cooling system, circa 1.0 million gallons capacity, was remarkable when the previous levels of hypochlorite dosed to achieve unsatisfactory control is considered.

The TVC results illustrate the value of duplicate sampling, since they reveal a level of variability between samples taken 10 min apart which would have gone unnoticed using a less rigorous protocol, with a concomitant reduction in the potential significance of the data obtained. Comparison of the sampling techniques shows that dip slide counts are generally one or two orders of magnitude lower than TVC results. This finding and the variance in TVC results at 10-min intervals may necessitate reviewing the current bacterial testing protocols. It should also be noted that whilst dip slides can be used to measure underlying bacterial trends they are not a substitute for quantitative laboratory-based TVCs.

CONCLUSIONS

The evaluation of mixed oxidant solutions replacing oxidising (hypochlorite or bromine) and non-oxidising biocides for maintenance of a disinfection residual, showed that the mixed oxidant solution:

1. Eliminated the need for additional biocides.
2. Maintained aerobic bacterial counts in the cooling water below CTB, TIMET and L8 specifications; the ability to keep low bacterial counts presents advantages in maintaining cooling surfaces free of biofilm.
3. Was easy to use with standard redox controllers; specific ion electrodes maintained FAC reserves within 0.1 ppm residual.
4. Eliminated existing biofilm and totally inhibited the build-up of new biofilm. This has the benefit of eliminating under biofilm corrosion by iron and sulphate reducing bacteria.
5. When used in conjunction with Waterman's stabilised phosphate and azoles patented programme for steel and copper protection, the mixed oxidant solution did not adversely affect corrosion rates within industry norms on steel, stainless steel and copper.
6. Is cost-competitive with chlorine gas and lower than the cost of sodium hypochlorite, chlorine dioxide or bromine; no hazardous chemicals also means no COSHH implications, no risk assessments, reduced safety equipment and training costs, and reduced liability exposure.
7. The short-lived and non-toxic nature of activated water ensures that environmental discharge, storage, handling and spillage problems are all eliminated.
8. The technology has significant potential across a wide range of current applications that use high value consumable products that give significant environmental impact.
9. TIMET UK Ltd. has now adopted this technology on all site cooling towers.

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PART II

DEVELOPMENT OF MODERN TECHNOLOGIES OF SPECIAL WATER TREATMENT FOR USE IN VARIOUS AREAS OF SCIENCE, INDUSTRY AND PUBLIC HEALTH

FIBROID SORBENTS FOR WATER PURIFICATION

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ABSTRACT

Polyester filters are produced and widely used in various countries for removal of dust from air. The process of filter production includes their treatment by acrylonitrilic emulsion for improving their mechanical characteristics. We have developed the technology of modification of polyester filters for production of ion-exchange and carbonic fibroid sorbents. The production of cation-exchange sorbents involved the treatment of ppolyester fibroid filters by a 20-25% solution of $NH_2NH_2 \cdot H_2O$ at 70-90^{o}C and a 5% solution of NaOH at 40^{o}C. Anion-exchange sorbents were made by treatment of cation-exchange sorbents with a 1-5% solution of polyethylenimine at ambient temperature. These new types of sorbents are used for the removal of radionuclides, heavy metal ions, and organic contaminants from wastewater and drinking water. We have investigated the main properties of these sorbents and their ability to remove ^{57}Co, ^{60}Co, ^{65}Zn, ^{89}Sr, ^{90}Sr, ^{134}Cs, ^{137}Cs, and other radionuclides, heavy metal ions (Zn, Ni, Cu, Sb, Pb, Cd, Cr, U, etc.), organic molecules M (pesticides, phenols, dioxins, benzene, toluene, etc.), radio-labeled organic molecules M-^{32}P, M-^{131}I, M-^{99}Mo+^{99m}Tc, M-^{14}C, etc. The influence of pH and concentration of K^+, Na^+ and other ions on percentage removal, as well as the decrease of saturation capacity with increasing number of regenerations and other characteristics are described. The static exchange capacity is 1-2 meq/g for cationic sorbents and 0.5-1 meq/g for anionic sorbents. The capacity of the carbonic sorbents for removal of benzene is 100 mg/g. The developed sorbents are effective in removing low concentrations of contaminants from water (lower than 100-200 mg/L).

A. Omelchenko et al (eds.),
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At present, newly developed ion-exchange and carbonic sorbents are used as drinking water filters and mini-systems for removing organic and inorganic contaminants. The sorbents described are also used for removing heavy metal ions from effluents from electroplating plants (Zn, Ni, Cd, Cr, Sb, Sn, etc.), match-producing plants (Zn, Cr, Sb, etc.), leather- and skin-treating plants (Cr), and for removing oil from car-wash wastewaters.

INTRODUCTION

Purification of wastewater and drinking water from radionuclides, heavy metal ions and organic contaminants is one of the most important problems at present. The ion-exchange method employing various types of resins and fibroid sorbents is widely used for solving this problem.

The high rate of the sorption process, effective regeneration and low value of pressure drop over the sorbent layer (Kragten 1978, Zverev 1981) represent advantages of the fibroid ion-exchange sorbents compared to resins. The specific surface of the fibroid sorbents is $(2\text{-}3)\times10^4$ $m^2/$ kg, *i.e.*, about 100 times larger than that of resins (~100 m^2/kg). Therefore, the sorption process on the fibroid sorbents is much faster than that on the resins. The main drawback of the fibroid sorbents is their very low density ranging from 50 - 200 kg/m^3.

Most manufactured fibroid filters are mainly used for removal of dust and aerosols from air, as they do not have ion-exchange properties. The objective of this study was to develop the technology of production of dust fibroid filters to produce fibroid filters having ion-exchange properties. This approach is more economically sound in many cases since it does not require construction of new plants.

One of the widely produced dust filters is the polyester fibroid filter. The manufacturing process includes treatment of the filters by an acrylonitrilic emulsion for improving their mechanical characteristics. This technological step can be used for production of the cation- and anion-exchange sorbents.

MATERIALS AND METHODS

Polyester fibroid filters with a surface density of 0.27 kg/m^2 and a thickness of 10 mm were utilized as a raw material for making the ion-exchange sorbents. The mass of the polyacrylonitrilic layer covering the surface of the fibers was 15% of the total mass of the filter. To produce ion-exchange sorbents, 1-10% solutions of NaOH and 0.5-5% solutions of polyethylenimine $(NHCH_2CH_2)_x[(CH_2CH_2NH_2)CH_2CH_2]_y$ were used for treatment of the polyester fibroid filters.

To optimise the production process, a 1 mM $CuCl_2$ solution labelled with ^{64}Cu and a $K_2Cr_2O_7$ solution (pH 2) labelled with ^{51}Cr were used in trials of the cation- and anion-exchange sorbents, respectively. ^{64}Cu and ^{51}Cr radionuclides were made by irradiating $CuCl_2$ and $K_2Cr_2O_7$ using the nuclear reactor at the Institute of Nuclear Physics (Tashkent, Uzbekistan). A Ge(Li)-detector with resolution about 1.9 keV at 1.33 MeV and a 4096-channel analyser were used to detect γ-quantum from the radionuclides. The areas under the γ-peaks of the radionuclides ^{64}Cu (half-life $t_{1/2}$ = 12.8 h and energy of the γ-peak E_γ = 0.511 MeV) and ^{51}Cr ($t_{1/2}$ = 27.72 days and E_γ = 0.320 MeV) were measured to calculate the amount of Cu and Cr, respectively.

The characteristics of these and other radionuclides used to label various ions and organic substances in the investigation of sorbents are presented in Table 1.

Table 1. Characteristics of radionuclides used as labels

Substance	Radionuclide	$t_{1/2}$	E_γ , MeV
M-^{32}P	^{32}P	14.3 days	E_β=1.7
Cr(VI)	^{51}Cr	27.73 days	0.320
Co(II)	^{60}Co	5.27 years	1.17, 1.33
Ni(II)	^{65}Ni	2.5 h	1.480
Cu(II)	^{64}Cu	12.7 h	0.511
Zn(II)	^{65}Zn	244.1 days	1.115
Br(I)	^{82}Br	35.3 h	0.776
Sr(II)	^{89}Sr	50.5 days	0.909
M-^{99}Mo+^{99m}Tc	^{99}Mo+^{99m}Tc	66 h (6 h)	0.140
Cd(II)	^{115}Cd	53.5 h	0.336
Sb(II)	^{124}Sb	60.2 days	1.691
M-^{131}I	^{131}I	8.04 days	0.364
Cs(I)	^{134}Cs	2.07 years	0.605

The exchange capacity Q, meq/g, may be calculated by Eq. (1):

$$Q = (A_0 - A_e)/(A_0 - A_B) \times B/W, \qquad (1)$$

where B is the amount of carrier, meq; W is the weight of exchanger, g; A_0 is the count rate of the original solution, A_e is the count rate of the solution at equilibrium, A_B is a background count.

The distribution coefficient K_d and percentage adsorption P could be calculated by Eqs 2 and 3, respectively:

$$K_d = ((A_0 - A_B)/ (A_e - A_B) - 1) \times V/W, \qquad (2)$$

$$P = (1 - (A_e - A_B) / (A_0 - A_B)) \times 100, \qquad (3)$$

where V is the total volume of the solution, mL. The processes of ion sorption from water were studied in dynamic conditions using columns of diameter 12 mm containing 1 g of sorbent.

RESULTS AND DISCUSSION

The kinetics of saponification of the fibers and the changes in the linkage quality between polyester fibers and the polyacrylonitrile layer after chemical treatment of the filters were studied in the presence of 1-10 % NaOH. The results obtained in the presence of 5% NaOH are demonstrated in Figures 1 and 2. It is notable that the filter capacity increases upon increasing the temperature of the treatment solution and the duration of treatment, however the linkage between the polyester fibers and the polyacrylonitrile layer is attenuated and the layer is scattered. Thus, treatment by a 5% solution of NaOH at 45-50°C for 1 h was selected as optimal for production of the cation-exchange sorbents. The exchange capacity of the sorbents with respect to Cu^{2+} was 0.25 meq/g.

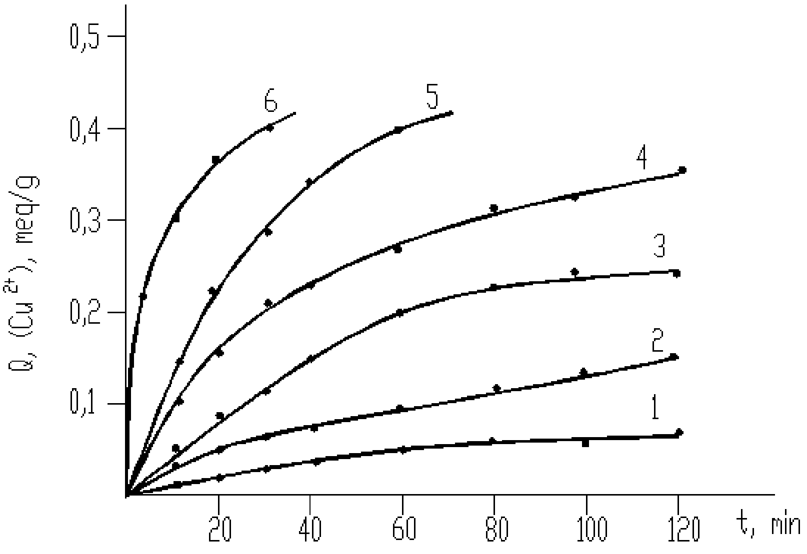

Figure 1. Kinetics of saponification of the fibers in 5% NaOH solution at 25°C (1), 30°C (2), 40°C (3), 50°C (4), 70°C (5) and 90°C (6).

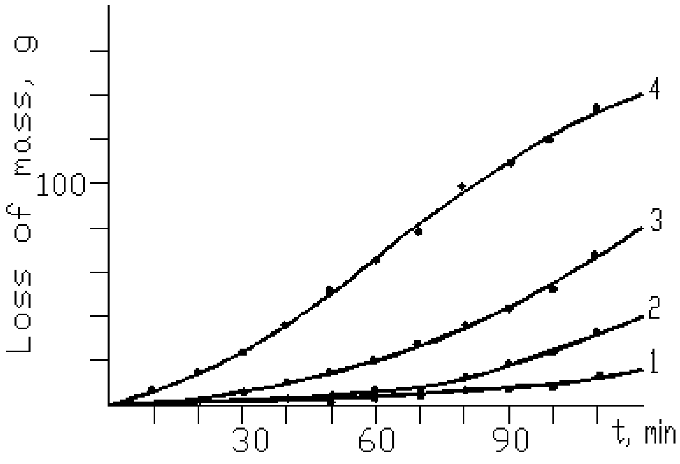

Figure 2. Change of the linkage quality between polyester fibers and the polyacrylonitrile layer after chemical treatment during *t* minutes at 30°C (1), 50°C (2), 60°C (3) and 70°C (4).

Anion-exchange sorbents were made by treatment of cation-exchange filters in the H-form by an aqueous solution of polyethylenimine and the imino groups are attached to the carboxy groups by electrostatic forces. The kinetics of formation of anion-exchange groups at concentrations of polyethylenimine ranging from 0.5-5% and temperatures ranging from 20°-70°C were studied. Fig. 3 demonstrates the kinetic curve at 40°C in the presence of 1% polyethylenimine, whereas Fig. 4 shows the dependence of exchange capacity on concentration of polyethylenimine at 40°C and 8 h treatment time. The treatment of the cation-exchange sorbents by 1% polyethylenimine at 40°C during 8-10 h was considered optimal for production of the anion-exchange sorbents. The exchange capacity of the sorbents with respect to Cr^{6+} was 0.45 meq/g.

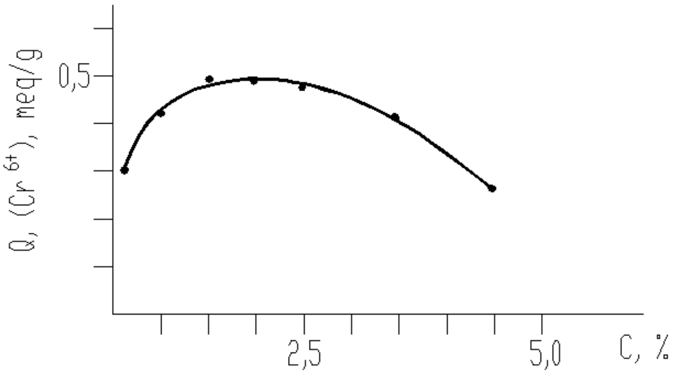

Figure 3. Kinetics of formation of anion-exchange groups at 40°C in 1% polyethylenimine.

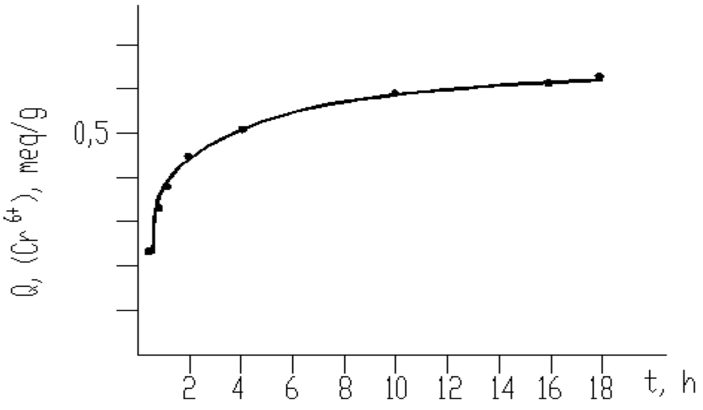

Figure 4. Dependence of exchange capacity on concentration of polyethylenimine at 40°C.

Removal of heavy metal ions (Zn, Ni, Cu, Sb, Co, Cd, Cr, etc.) and organic molecules labelled by radionuclides (M-^{32}P, M-^{131}I, M-^{99}Mo+^{99m}Tc, etc.) from water using fibroid sorbents was studied. The dependence of the distribution coefficient K_d for various ions and organic substances on the pH of solutions is presented in Table 2.

Table 2. Distribution coefficient K_d (mL/g) for various ions and organic substances (C_o = 10 mg/L, V=50 mL, W=0.5 g)

Substances	*Distribution coefficient at various pH*									
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
Co(II)	*3000*	*2600*	*2300*	*2000*	*1700*	*1000*	*126*	*138*	*150*	*160*
Ni(II)	125	600	870	920	990	750	430	510	780	1000
Cu(II)	140	400	600	480	400	560	650	560	460	340
Zn(II)	230	2000	4000	5000	4000	1900	1700	1400	900	800
Sr(II)	11	25	45	100	300	1000	1900	8000	6000	900
Cd(II)	980	830	680	520	380	240	97	75	46	17
Sb(II)	260	190	150	130	120	120	115	90	70	35
Cs(I)		100	200	900	1900	3200	4000	4000	1500	11
Cr(VI)	200	150	100							
M- ^{32}P		3200	3000	2700	2500	1900	1100	300	150	
M-^{131}I		3100	2800	2600	2300	2100	1900	500	150	
^{99}Mo+^{99m}Tc			2900	2800	2400	2300	2000	500	140	

The specific behaviour of pH-dependence of K_d for Co(II), Ni(II) and Cu(II), *i.e.*, the existence of more than one maximum for the K_d vs. pH curves, can be explained by the changing relationship between ionic forms of the corresponding metals in solution with pH due to hydrolysis (Ashirov 1983). The influence of additional foreign cations Na^+ and K^+ on the adsorption of different metals at pH 7 is presented in Table 3.

Table 3. Influence of additional foreign cations Na^+ and K^+ on the distribution coefficient K_d (mL/g) of different ions at pH 7.

Ion	Na^+		K^+		Na^++ K^+
	10 mg/L	100 mg/L	10 mg/L	100 mg/L	100+100 mg/L
Co(II)	130	140	130	140	140
Ni(II)	510	300	520	420	500
Cu(II)	600	460	550	530	530
Zn(II)	1700	800	1700	800	800
Cd(II)	38	34	50	32	20
Sb(II)	115	115	115	115	115

Adsorbed ions were eluted using 1M HCl at a flow rate of 2 mL/min and 1-mL aliquots were collected each time for radiometric measurements. Fig. 5 showing the plot of activity expressed in counts per minute (cpm) for corresponding aliquots vs. the volume of eluant exemplifies the elution profiles of copper, cobalt and cadmium. It can be seen that about 95% of the adsorbed ions were recovered by elution with 30 mL HCl. The dependence of capacity decrease, ΔQ %, on the number of sorbent regenerations is given in Fig. 6.

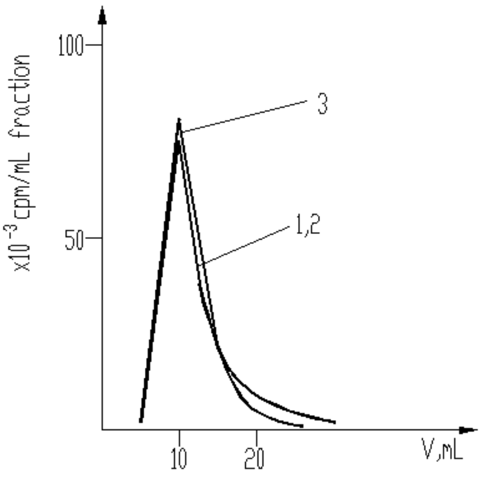

Figure 5. Elution profiles of copper, cobalt (1,2) and cadmium (3) vs. volume of eluant.

CONCLUSIONS

The above results show that the chemically modified polyester fibroid filters have satisfactory adsorption characteristics. These cation- and anion-exchange filters can be used for removal of metal ions (Zn, Ni, Cu, Sb, Co, Cd, Cr, etc.) and organic compounds (M-^{32}P, M-^{131}I, M-^{99}Mo+^{99m}Tc, etc.)

from water. The capacity of the cation-exchange sorbents is 0.25 meq/g (Cu^{2+}) and that of the anion - exchange sorbents is 0.45 meq/g (Cr^{6+}).

At present, these newly developed ion-exchange sorbents are used in drinking water filters and mini-systems in wastewater treatment equipment for the removal of such organic and inorganic contaminants as oil (at atomic power stations, car-washing facilities, etc.), and heavy metal ions (at electroplating plants, match-producing plants, leather- and skin-treating plants).

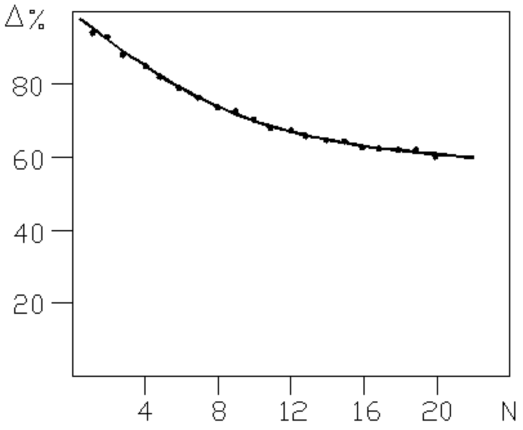

Figure 6. The decrease of sorbent capacity, ΔQ, vs. a number N of regenerations.

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USE OF IN-SITU OXYGEN CURTAIN TECHNOLOGY IN ENHANCED BIOREMEDIATION OF GROUNDWATER

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ABSTRACT

In-Situ Oxygen Curtain (iSOC™) is an ingenious oxygen delivery technology based on inVentures' patented Gas inFusion™ technology - a unique method of infusing supersaturated levels of dissolved gas into liquids. At the heart of the iSOC™ is the proprietary structured polymer mass transfer device. A microporous hollow fiber provides an enormous surface area for mass transfer- in excess of 7000 m^2 per m^3- and it is hydrophobic. Maintaining a gas at lower pressure than liquid ensures that ultra efficient mass transfer takes place without the formation of bubbles. When suspended in existing monitoring wells, the iSOC™ infuses high levels of oxygen into groundwater, without bubbles, and with a very low decay rate at atmospheric pressure. By simply connecting a regulated supply of compressed oxygen to a small diameter flexible tube leading to the iSOC™, high levels of supersaturated, nascent oxygen transfer takes place in the surrounding groundwater. For example, a regulated iSOC™ can infuse over a pound of dissolved oxygen per month at a supersaturated, bubbleless 70 ppm when the saturated depth is 20 feet, with resultant significantly increased oxygen concentration for bioremediation down gradient. Once oxygen is introduced into the groundwater, the laws of mass transport generally apply. The greatly enhanced level of dissolved oxygen in groundwater addresses dissolved-phase petroleum hydrocarbon contamination as well as sorbed material in the saturated, capillary fringe, and smear zones. The iSOC™ can create an enhanced O_2 curtain or barrier to prevent contamination migration or it can be used for the treatment of so-called "hot spots".

A. Omelchenko et al (eds.),
Modern Tools and Methods of Water Treatment for Improving Living Standards, 109–113.

INTRODUCTION

In recent years, bioremediation technologies have been recognised as some of the most cost effective and environmentally friendly processes for solving ecological pollution problems. Applications of bioremediation technologies now account for a significant number of ongoing clean-up projects worldwide.

In-situ groundwater bioremediation is a treatment process that enhances the growth and reproduction of naturally occurring microorganisms to stimulate biodegradation of organic hazardous substances into less toxic or nontoxic substances. In-situ groundwater bioremediation can effectively degrade organic contaminants, such as fuels, into harmless products - mainly carbon dioxide and water.

In-situ bioremediation processes treat the contaminated groundwater on-site, without removing and treating water at another location. The rate of biodegradation of organic contaminants by microorganisms can be enhanced by increasing the concentration of electron acceptors in groundwater, e.g., oxygen, which is the main electron acceptor for aerobic bioremediation.

Efficiency of enhanced aerobic bioremediation in terms of cost and performance largely depends on the mechanism of oxygen introduction into the groundwater.

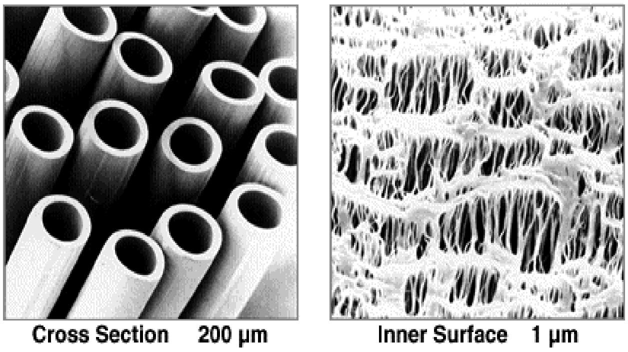

Figure 1. Microporous hollow fiber.

iSOC™ TECHNOLOGY

iSOC™ is an ingenious oxygen delivery technology based on inVentures' patented Gas inFusion™ technology - a unique method of infusing supersaturated levels of dissolved gas into liquids. At the heart of iSOC™ is the proprietary structured polymer mass transfer device.

Microporous hollow fiber (Fig. 1) provides an enormous surface area for mass transfer - in excess of 7000 m^2 per m^3 - and is hydrophobic (will not pass water). Maintaining a certain gas pressure ensures that ultra efficient mass transfer takes place without the formation of bubbles. When suspended in existing monitoring wells, the iSOC™ (Fig. 2) infuses high levels of oxygen into groundwater, without bubbles, and with a very low decay rate at atmospheric pressure.

Figure 2. iSOC™.

Gas inFusion™ technology is designed to:

(a) Conduct rapid, no bubble gas transfer (infusion)
(b) Create dissolved oxygen concentrations of hundreds of ppm
(c) Allow long-term retention of extremely high dissolved oxygen levels
(d) Virtually eliminate dissolved oxygen losses to atmosphere
(e) Achieve gas transfer efficiencies 10 times better than best conventional methods
(f) Allow specifically designed mass transfer devices.

iSOC™ ENHANCED REMEDIATION

iSOC™ supersaturates well with bubbleless, low decay dissolved oxygen at 40 to 200 ppm depending on groundwater depth allowing natural convection current to fill the well with uniform dissolved oxygen. As dissolved oxygen is dispersed around the well into groundwater, soil or fractured bedrock, enhanced bioremediation removes organics (hydrocarbons).

iSOC™ applications are easy, flexible, and may be designed to meet a variety of remediation objectives, such as:
(a) Creation of O_2 barrier at leading edge of the contaminant plume
(b) Avoids boundary litigation
(c) Protects off-site receptors
(d) Source treatment
(e) Reduces contamination levels with supersaturated O_2 at heart of the plume
(f) Rapid, localized remediation of low-level contamination in existing monitoring wells
(g) Cost effective, passive enhancement of natural biodegradation
(h) Accelerates site closure.

iSOC™ has established itself as an extremely useful tool in groundwater enhanced bioremediation due to the following advantages:

(a) iSOC™ infuses 4 to 10 times more dissolved oxygen than any other competitive technology. iSOC™ can be used without interrupting normal activities on a construction site
(b) iSOC™ is small, predictable, simple, and can be easily moved to a new injection point or new site
(c) iSOC™ can be installed in existing 2-inch monitoring wells
(d) iSOC™ does not require electricity and is connected only to a standard oxygen cylinder

iSOC™ INSTALLATION AND CONTROL

The iSOC™ Probe consists of a SS316 stainless steel casing and screen that houses a microporous, hydrophobic, hollow fibre membrane, all materials being highly tolerant to most media. The iSOC™ probe is 1 5/8” in diameter and 15” in length, with barbed connector for 6-mm polyurethane tubing, and lifting ring. It sits at the bottom of the well. Oxygen is transferred across the membrane by diffusion. Welding grade compressed oxygen gas is infused at 15mL/min and 12 psig (~ 56 gm O_2/day/well). One oxygen cylinder is used within approximately 2 to 3 weeks for 7 wells.

Single and triple control panels, stainless steel construction specifically designed and manufactured for iSOC™ system use, monitor and control gas flow and pressure. The single-unit control panel is 3"×9"×8" and weighs 3 lbs. The triple-unit control panel is 3"×21"×8" and weighs 8 lbs.

Installation of the iSOC™ system is very simple (Figure 3):
(a) Connect gas supply to the iSOC™ system panel
(b) Connect the iSOC™ to the system panel
(c) Turn on gas
(d) Adjust & set gas flow
(e) Lower the iSOC™ into well
(f) Adjust and set gas flow
(g) Monitor dissolved oxygen levels.

iSOC™ DEMO CASE STUDY

An enhanced bioremediation project using the iSOC™ system was conducted at an active service station. Site characteristics were represented by the following data:
(a) Sand and silty sand underlain by silts and clays
(b) Depth to groundwater: 6 – 12 ft
(c) Groundwater velocity: 0.3 – 0.4 ft/day, gradient 0.028
(d) Historical groundwater methyl tertiary butyl ether (MTBE) concentrations indicate slugs moving through the aquifer

(e) Recovery wells yield up to 1 gpm; existing air stripper/GAC system has iron clogging problems (ferrous iron ~30-80 mg/L). Baseline conditions were summarised as the following:
(a) 28 wells (3 existing and 25 new) sampled for baseline event
(b) Wells sampled and analyzed for benzene, toluene, ethylbenzene and xylene (BTEX), tertiary butyl alcohol (TBA), biological parameters, pH, temperature, & conductivity
(c) Baseline MTBE concentrations range from 3 to 7 ppm, TBA from 20 to 30 ppm, and benzene up to 0.6 ppm
(d) Baseline event shows aquifer in anaerobic and reduced conditions

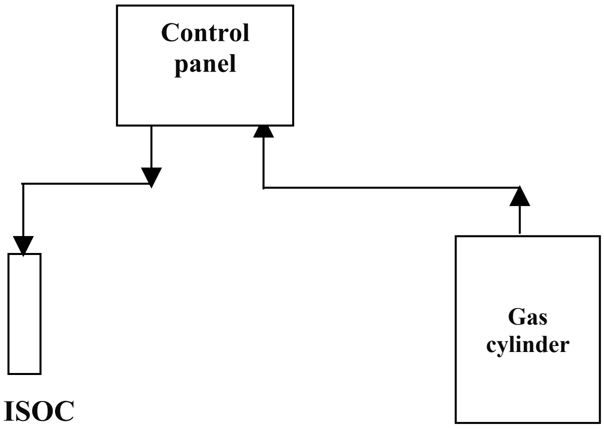

Figure 3. iSOC™ system setup.

Three months after the iSOC™ system was installed, an effective barrier of dissolved oxygen was established and remained effective in attenuating MTBE, TBA and benzene throughout the 6-month study period. Significant concentration reductions downward of the iSOC™ oxygen barrier were comparable for shallow and deep piezometers: MTBE - 89%, TBA - 54%, benzene - >96%. The data indicates aerobic degradation of MTBE downward of the iSOC™ oxygen barrier and possible anaerobic biodegradation outside of the test location.

ELECTROCHEMICALLY-STIMULATED SORPTION AND SORPTION-MEMBRANE METHODS FOR REMOVAL OF IONIC IMPURITIES FROM WATER

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INTRODUCTION

Purification of water from ionic impurities is a process of significant importance among modern technologies. Among the large number of different methods, which are used for purification of solutions, reagent and sorption purification methods are the most popular. Reagent purification consists of the addition of a chemical reagent to the solution to be purified. This reagent is able to bind the pollutant into a new chemical compound, which can be easily removed from the reaction mixture. The application of reagent purification is expedient at high concentrations of pollutant, but the degree of purification, in general, is not sufficient. A much higher degree of purification can be achieved by application of sorption methods for removal of pollutants. Thus, the widely used application of ion-exchange resins allows high degrees of water purification from almost all kinds of ionic water pollutants. However, the main disadvantage of ion-exchange technologies for water purification is the necessity to use additional chemical reagents (e.g., acids and alkalis) for the regeneration of the sorbents and that results in large quantities of wastewater. According to the data in (Grebenyuk 1978), the purification of 1 m^3 of water solution by ion-exchange resins produces 10 m^3 of water polluted by the products of interaction of the ion exchangers with acids and alkalis, which were used for regeneration.

More promising, from the environmental point of view, are the electrochemical methods, which do not require the introduction of additional chemical reagents. Here all the necessary and generally non-toxic reagents are produced as a result of electrochemical reactions under the application of an

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electric field to the solution. One of the most popular and widely used methods of purification of water solutions under the influence of an electric field is the method of electrodialysis. This method is rather effective in water desalination processes for removal of cations of monovalent metals and simple inorganic anions. However, during the treatment of solutions containing impurities of organic compounds and cations capable of forming insoluble hydroxides, its effectiveness drastically decreases as a result of the fouling of the ion-exchange membranes. At present, the more universal electrochemically-activated processes for water processing, which allow the removal of a wide variety of pollutants, are being intensively investigated. It has been demonstrated that an electric field with intensity $E = 20\,kV/m$ and higher applied to water solutions causes a significant decrease of hardness, opacity, coloration, concentrations of toxic ions of heavy metals and bacteria. The mechanism of such influence is rather complex, nevertheless, it is thought that the following consecutive electrochemically-activated processes take place: electrophoresis → polarized coagulation → hydroxide formation → flocculation → flotation (Vilinskaya 1987).

These processes are rather effective for the removal of organic compounds and metal ions, which form insoluble hydroxides. These processes are less effective for the removal of anionic impurities from water solutions and almost ineffective for the removal of monovalent ions of alkali metals. Nevertheless, in many cases, the application of electrochemical activation methods, for example, for purification of potable water, can be quite effective. Despite their obvious viability for technical realization, such methods are not widely used in water processing due to high-energy consumption and rather complicated design of the apparatus, which requires electric fields of high intensity.

Significantly lower energy consumption and high efficiency can be obtained by the application of electrochemically-stimulated sorption for water purification. The methods of electrochemically-activated sorption are based on the fact that, on contact with one electrically charged electrode, electroconducting sorbents can change the value of their polarization and sign of surface charge (Khabalov et al. 1989). Both the polarization and surface charge determine the sorption activity towards ions or polarized organic compounds. (The term «electrochemically-stimulated sorption» is used in the current paper. According to Grevillot (1989), it can be accepted that a «pure» electrosorption process takes place only when the interaction of absorbed compound with the charged surface of a polarized sorbent is not complicated by interaction of this compound with the products of electrochemical reactions.) In contrast to the method of water purification by means of electrochemical activation, the method of electrochemically-activated sorption allows the removal from aqueous solutions of cations of metals, which form insoluble hydroxides, as well as cations of monovalent metals and anions, similar to the method of ion-exchange sorption. The influence of the electric field on the surface charge of the electroconducting sorbent allows optimization of the sorption conditions within a pre-determined range. However the most important advantage of electrochemically-stimulated sorption is the possibility to conduct non-chemical regeneration of sorbents by changing the value and sign of the surface charge.

It is important to note that polarized conductive sorbents are able to function as three-dimensional (3D)-electrodes (Wolfkowich 1984). This allows the use of some electrochemical processes occurring on the surface of conductive sorbents to control sorption processes. For example, the application of a 3D-sorption electrode for water electrolysis allows control of the acidity in the sorbent phase. In other words, the application of sorption electrodes for water electrolysis allows acidification and alkalinization of the electrolyte near the anode and cathode, respectively. This can be described by the following equations:

$$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2 \qquad \text{(cathode)}$$

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad \text{(anode)}$$

The control of the acidity is of importance for ion-exchange sorption because it allows the equilibrium of the ion-exchange reaction to be shifted towards either increase or decrease of the sorption ability in relation to ionic components in solution. Of course, the application of electrochemically-activated sorption charges undesirable components as well. Thus, the range of removable particles is restricted to ions or compounds easily polarized in electric fields. A significant number of organic and inorganic compounds have such properties. Thus, electrochemically-activated sorption can be used in a wide range of applications.

In contrast to other electrochemically-activated processes for water purification, including electrodialysis, the electrochemically-controlled sorption processes do not require high electric fields. To polarize the sorbent, it is enough to apply a voltage ranging from hundreds of millivolts to several volts depending on the cell design and electroconductance of the purified solution. This is due to the fact that, in the process of electrochemical sorption, energy is consumed only for reconfiguration of the double electric layer and generation (as a result of water electrolysis) of H^+ or OH^- ions. The number of these ions equals the number of absorbed ones. All this defines the significant advantages of electrochemically-stimulated sorption with respect to energy consumption as compared to the other above-mentioned methods.

Some devices utilizing polarized sorbents for water treatment are described in the literature. In general, conductive carbon materials, such as activated carbon (Khabalov et al. 1989, Grevillot 1989), powdered graphite (Patent USA 1974) or a novel material carbon aerogel (Pekala et al. 1988, Farmer et al. 1996), which are able to effectively remove both organic compounds and ions, are employed. Unfortunately, ion-exchange resins, which are widely applied for removal of ionic components from water solutions, cannot be used for electrochemically-stimulated sorption because they have extremely low conductivity and are not polarized on contact with the electrodes. The effect of electric current on ion-exchange resins results in the generation of acid or alkali near the electrodes, which in turn influences the sorbent. This results in extremely high-energy consumption and low effectiveness. Recently, the possibility of the effective influence of polarization on the sorption properties of inorganic proton-conductive ion-exchange materials, e.g., phosphates of multivalent metals, having significant proton conductivity was shown. It was found that proton-conducting sorbents are able to function as 3D-sorption electrodes. The study of sorption by polarized phosphate sorbents has revealed an increase of sorption capacity up to 200 %, significant improvement of kinetic characteristics and increase of sorption rate (Grevillot et al. 1999).

Despite the obvious efficiency of electrochemically-stimulated sorption in water purification, the main obstacle for its wide application is the fact that currently, dispersed sorbents, not electrochemically-optimized ones, are used for the preparation of sorption electrodes. If dispersed sorbents are used in the form of layer beds, the problem of poor electric contact between particles and the current collector or polarizing electrode is made worse by the similarly bad contacts between the particles themselves. This limits the value of exchange currents between sorbent granules and increases the time required to establish the equilibrium of the sorption. It leads to a significant deceleration of sorbent electrochemical stimulation.

The second disadvantage of the application of dispersed sorbents is the impossibility of their use to produce mechanically durable monolithic constructive elements. The use of sorbents (as a layer bed) in electrochemical devices requires solution of the problem of reliable current feed to the sorbent granules, because the contact surface is small and the electrode reactions, which do not take part in the process of electrochemically activated sorption, may take place mainly on the electrode. Thus the effectiveness of the process is decreased. The poor contact between particles in the bed layers also causes significant variations in the sorption activity of the different layers.

The third disadvantage for the application of standard sorbents in electrochemically-stimulated sorption is their porous structure. Usually, to increase the sorption capacity of sorbents, the specific surface area of the sorbent should be maximized during synthesis. The increase of the specific surface is connected to the decrease of the pore sizes of the starting material. Therefore most carbon sorbents, for example active carbons, are microporous. However, it is known (Khabalov et al. 1989), that pores with a diameter less than 200 Å are not electrochemically active, because the formation of a double electric layer is not possible in such types of pores. Therefore, the majority of the carbon sorbent surface cannot be used in electrochemically-controlled sorption processes. It is noteworthy that carbon materials are not totally suitable for the preparation of sorption electrodes, because they have extremely low sorption activity towards non-hydrolyzing metal cations, which should be removed during the water purification process. Inorganic ion exchangers can be promising materials for electrochemically-activated sorption for the removal of metal cations. These materials are prepared from phosphates of multivalent metals. They have significantly higher cation-exchange activity; however these sorbents, which are prepared in the form of dispersed particles, have the same disadvantages as carbon materials.

Taking into consideration the above-mentioned facts, it is possible to formulate some basic requirements for materials, which can be used as effective sorption electrodes in the process of water purification from ionic impurities and easily polarized compounds. They are as follows: (i) comparatively high value of specific surface and rather large diameter of pores (macropores); (ii) the presence of functional groups, which on dissociation can form a surface charge and facilitate ion exchange adsorption; (iii) sufficient electroconductance (electron or proton); (iv) ability to form mechanically durable structural elements of relatively large size and different shape.

Among the wide range of new industrially produced materials, the porous ceramics used for manufacturing inorganic membranes best meets the above requirements. Porous ceramics are based on oxides of multivalent metals, e.g., Al_2O_3 and ZrO_2. They are chemically stable over a wide range of pH and have amphiphilic properties. These compounds are able to adsorb both cations and anions by the ion exchange mechanism. The porous structure of such materials can be changed over a wide range, but the lower value is limited and, as a rule, the average diameter of pores is more than 0.1 μm. The macroporous structure and comparatively high value of specific surface (up to 10-20 m^2/g) allows consideration of such materials as prospective sorbents with good kinetic characteristics. Moreover, the high total porosity (up to 50 %) allows their use as a matrix for the preparation of composite sorbents having properties predefined by incorporation of other sorption-active components into the pore volume. For example, incorporation of phosphates of multivalent metals into the volume of the porous ceramic matrix increases the cation-exchange capacity. Ceramics can acquire electroconductive properties through some modifications, for example, by precipitation of pyrolytic carbon or metals. The possibility of control of the porous structure should also be considered. Material with a predefined porous structure can serve not only as a sorption electrode, but also as a membrane filter for removal of water impurities of relatively small size (more than 0.1 μm) including bacteria. It is noteworthy that porous ceramic materials can serve as a support for materials with electrocatalytic properties and can be used for oxidation of organic compounds into water and carbon dioxide by electrochemical oxidation. Therefore, it is possible to construct new multifunctional materials for water purification, which are able to remove impurities by simultaneous sorption, membrane filtration and catalytic transformation.

All the above provides the foundation for the given study. One of the main objectives was to assess the effectiveness of electrochemically-activated sorption processes for purification of some industrial solutions from ionic impurities. For this, the following experiments were conducted: (i) preparation of the sorption materials on the basis of porous oxide ceramic, (ii) assessment of sorption activity of the prepared materials with respect to the basic components of some industrial solutions, (iii) determination of the influence of electric polarization on the adsorption ability of the prepared materials, and (iv) investigation of electrochemically-stimulated removal of ionic impurities from solutions mimicking industrial ones.

Another objective was to develop new electrosorption materials in the form of plates. Such electrosorption membranes are especially promising for large-scale application of electrosorption technology for removal of ions from aqueous solutions. Firstly, the membranes can be arranged as plate-and-frame modules, which offer significantly higher volume to flow ratios than the tubular membrane modules. Secondly, it may be significantly easier to supply evenly distributed electric current to the plate surface than to the tube one. During the development of the composition and methods of synthesis of the planar electrosorption membranes, it was taken into account that the final product should possess the following properties: (i) ability to adsorb ions by ion exchange processes, (ii) electroconductivity, (iii) porosity, (iv) good mechanical properties.

NEW INORGANIC MATERIALS AND ELECTROCHEMICALLY-STIMULATED SORPTION

Flat porous ceramic was used as a support for the preparation of composite electrosorption materials. It is known that ceramic materials prepared from oxides of polyvalent metals possess adsorption and ion exchange properties both for cations and anions. Thus, such materials can be used as electrosorption membranes, if they are electroconductive. It is potentially possible to use electroconductive ceramic materials for the preparation of electrosorption membranes, but they are currently extremely expensive. Low cost ceramic electroconductive materials were produced by pyrolytic deposition of carbon on the surfaces of flat ceramic supports. Another limitation of metal oxide ceramics is their low ion-exchange capacity. To increase the ion exchange capacity of ceramics, high sorption capacity compounds were impregnated into the porous matrices of the flat supports.

Planar sorption electrodes were prepared using non-woven ceramic fiber-based materials as supports. For this, three types of ceramic papers K-ShieldBF Paper, Kaowool 500 Grade Paper, and Kaowool 700 Grade Paper prepared from $A1_2O_3$ and SiO_2 ("Thermal Ceramic", USA) were used.

To confer electroconductivity onto porous ceramic materials, they were coated with a layer of pyrolytic carbon. The deposition of carbon was carried out in the gas phase by pyrolysis of natural gas (Belyakov and Paltchik 1995). The ceramic materials were placed in a quartz reactor through which natural gas was passed at a predetermined flow rate and then heated to the desired temperature (800-1000°C). Phosphates of Ti and Zr were selected as additional sorption-active components to be introduced into the porous matrices of the sorption electrodes. Selection was based on the following: (i) phosphates of Ti and Zr are well known inorganic ion exchangers, which possess relatively high ion-exchange capacity; (ii) phosphorus-unsaturated materials based on phosphates of Ti and Zr are capable of adsorption of both anions and cations from aqueous solutions; (iii) phosphates of Ti and Zr possess high ionic conductivity.

The method of insertion of zirconium phosphate into porous ceramic structures was based on impregnation of the porous materials with a crystalline sol of zirconium dioxide (Clearfield 1964). For preparation of the sol, small portions (2-3 mL) of a 25 % solution of ammonia were added to 1 L of a 1 M, heated and stirred, solution of $ZrOCl_2$. The temperature did not exceed 90°C. Each portion of NH_3 solution was added only after complete dissolution of the zirconium hydroxide precipitate. The addition of NH_3 solution was terminated once dissolution of the zirconium hydroxide precipitate took 20 min. The obtained raw sol was boiled using a reflux condenser for 25 h to allow formation of the crystalline structure. Then, the sol was cooled to ambient temperature and filtered. Ceramic materials were immersed in a 1 M sol of ZrO_2 prepared as described above. The immersion time was 12 h. After removal from the sol, the membranes were wiped with filter paper and placed into a 15 % solution of phosphoric acid for 15 h. This operation was aimed at the transformation of ZrO_2 into zirconium phosphate. After this, the membranes were rinsed with distilled water, air-dried for 24 h at room temperature and then for 2-3 h at 200°C.

The insertion of titanium phosphate was carried out by the following method. Ceramic support materials were immersed into a 1 M solution of $TiCl_4$ for 6 h. Then, the solution containing the ceramic materials was cooled to 0°C. The membranes were removed from the cold solution, wiped with filter paper and placed into a cold (0°C) 15 % solution of phosphoric acid for 15 h to transform the titanium salt in the pores of the ceramic into zirconium phosphate. Cooling of the solutions was necessary to deposit the titanium salt in the form of a mechanically strong and homogeneous gel. The membranes, obtained by this method, were thoroughly rinsed using distilled water, air-dried for 24 h at room temperature and further dried for 2-3 h at 200°C.

To achieve a maximum density of zirconium and titanium phosphate deposits inside the porous matrices, the impregnation operations described above were repeated up to 3 times.

Evaluation of sorption activity of the membranes under the condition of electrochemical activation was carried out as follows. The model solution was constantly stirred in a glass vessel, which contained two flat 50 mm x 20 mm electrodes. The distance between the electrodes was 10 mm. One of the electrodes was a piece of the prepared electrosorption membrane and the counter-electrode was made of graphite. Electric current was passed through the system for 0.5 h under potentiostatic conditions. After that, the solution was removed from the vessel and analyzed. In this way, the optimal composition and density of the electrosorption membranes were determined. The membranes that showed the best performance were selected for testing in the electrosorption cell that is shown in Fig. 1.

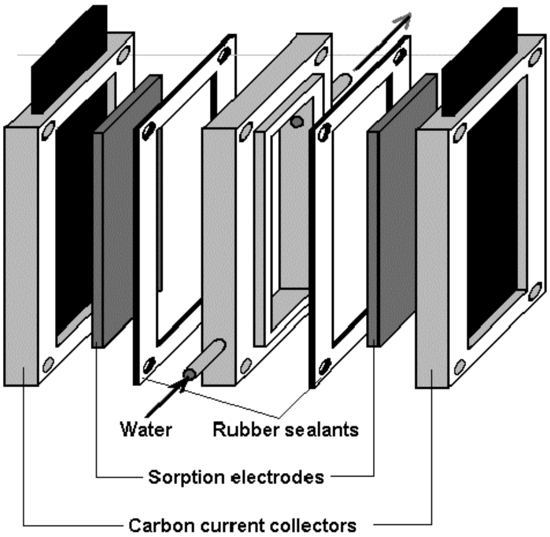

Figure 1. Electrochemical adsorption cell for testing the properties of electrosorption planar membranes.

The design of the cell allowed planar electrosorption membranes with dimensions 3 mm x 8 mm to be strongly pressed against graphite current collectors. The working solutions were pumped through the cell with pre-determined flow rates using peristaltic pumps. The volume of the working compartment of the cell was 25 cm^3. Rubber O-rings were used to keep the cell compartments under pressure.

The concentration of sodium ions was determined using a PAZ (Ukraine) flame photometer. Analysis of Ni, Ca and Mg ion concentrations was carried out by an atomic absorption method using a Pye Unicam 8800 (UK) spectrophotometer. The concentration of SO_4^{2-} was determined by titration with $BaCl_2$ solution in the presence of rhodizonate as indicator. Chloride ions were determined using ion selective electrodes (Radelkis, Hungary).

It was shown in preliminary experiments that the introduction of an electroconductive compound, such as pyrolytic carbon, allowed the use of phosphate-impregnated ceramic papers as effective electrosorption electrodes and control of their adsorption efficiency by direct application of electric current. The highest adsorption capacity and mechanical stability was observed for electrosorption membranes made of Kaowool 700 ceramic paper as the initial support material. These membranes were prepared by deposition of pyrolytic carbon at 900°C followed by three consecutive impregnations with zirconium or titanium phosphates.

A comparative study of the sorption properties of composite inorganic membrane materials based on ceramic paper filled with titanium and zirconium phosphate (three impregnations) was carried out to choose the optimal composition of the composite sorption materials. Since the molar ratio of phosphorus:metal in phosphates of zirconium and titanium determines their adsorption capacity towards cations and anions, electrosorption membranes with different molar ratios were produced and tested. The composition of phosphates of zirconium and titanium deposited into ceramic porous matrices was controlled by changing the contact time of the material with phosphoric acid during the phosphorization stage. One-molar NaCl solution was used for evaluation of sorption properties of the membrane without electrical polarization. The results are presented in Table 1. It was concluded that (i) the sorption capacity of composite membranes based on zirconium and titanium phosphates are practically identical; (ii) lower phosphorous content in the membrane reduces its sorption capacity towards cations and increases that towards anions; (iii) membranes with a molar ratio metal:phosphorous = 1:1 are optimal for simultaneous sorption of cations and anions.

Table 1. Sorption capacity of composite membranes prepared by the impregnation (three impregnations) of titanium (TiP) and zirconium (ZrP) phosphates into Kaowool 700 ceramic paper.

Molar ratio	Sorption capacity, mg/g			
	TiP		ZrP	
P:Me	Na^+	Cl^-	Na^+	Cl^-
1.5	124	35	115	30
1.0	95	63	92	60
0.5	60	70	55	65

The next step of the study was to prepare sorption electrodes from phosphate materials and to investigate their sorption properties under electrical polarization. Electrodes of different thickness were prepared by placing the phosphate impregnated ceramic paper in contact with current-collecting flat metal sheets. The results are summarized in Table 2. The following can be concluded: (i) the cathode polarization of the membranes increased their sorption capacity; (ii) the influence of polarization on sorption capacity is more pronounced for zirconium phosphate based materials (a rise in the sorption capacity up to 150 %); (iii) increase of the thickness of the sorption electrodes results in a lower specific sorption capacity; (iv) the influence of the type of current-collecting metal of the sorption electrodes on the sorption capacity was not specific; (v) impregnation with zirconium phosphate (ratio metal : phosphorous = 1:1) produces an optimal material for the preparation of sorption membranes.

Table 2. Influence of polarization and dimensions of sorption electrodes on their sorption capacity for Na^+ ions from 0.01N Na_2SO_4 solutions.

Thickness of sorption electrodes, mm	Sorption capacity, mg/g			
	TiP		ZrP	
	Without potential	E= - 0.3 V	Without potential	E= - 0.3 V
1	20	35	19	51
2	20	32	19	48
5	20	27	19	41
10	20	22	19	37

The last stage of optimisation of the active content of the sorption electrodes was multiple sorption-desorption testing under electrosorption conditions. The electrosorption cell shown in Fig. 1 was used for the testing. Tests were carried out utilizing a model solution of the following composition (in mg/L): 73.3 Ca^{2+}, 51.5 Mg^{2+}, 115 Na^+, 130 Cl^-, and 140 SO_4^{2-}. The results obtained for sorption electrodes containing titanium and zirconium phosphates (molar ratio P: Me = 1:1, three impregnations) are presented in Table 3.

Table 3. Degree of model solution purification by the electrosorption module equipped with titanium phosphate- and zirconium phosphate-containing electrosorption electrodes.

No. of sorption-desorption cycles	Degree or purification, %			
	TiP		ZrP	
	Without voltage	E = 10 V	Without voltage	E = 10 V
1	55	82	53	97
2	52	85	56	92
5	56	81	51	95
10	54	83	52	96

The following conclusions can be made from Table 3: (i) passage of an electrical current through the sorption cell greatly increases the degree of purification from ionic impurities; (ii) influence of polarization on the degree of purification is more pronounced for electrosorption membranes made of zirconium phosphate; (iii) the water purification characteristics of the cell do not change significantly over up to 10 sorption-desorption cycles, (iv) the results obtained have shown good performance of the electrosorption method for the purification of solutions with low content of salts (up to 0.5 g/L).

The flat sheet electrosorption modules were tested with industrial nickel-containing effluent and water sourced from a mine. Electrosorption tests with flat sheet electrodes were carried out using a model solution containing (in mM): 11 Ni_2SO_4, 8 NaCl, and 7 H_2SO_4.

Taking into consideration that Ni^{2+} and Na^+ can have different sorption and electrochemical behavior, the kinetics of sorption of these ions from separate salts was investigated. The results obtained with the electrosorption module equipped with zirconium phosphate-containing electrosorption membranes at E = 5 V are presented in Table 4.

Table 4. Removal degree (%) for sodium and nickel cations.

Cation	Removal degree at various times of sorption, %			
	5 min	10 min	20 min	30 min
Na^+	74	87	93	96
Ni^{2+}	46	59	73	80

The rate of sorption of Ni^{2+} was lower than that of Na^+. Therefore, in the study of desalination, using real electroplating effluents, the feed flow of solution in the electrosorption module was reduced to 100 mL/h. The results of treatment of nickel-containing industrial effluent are shown in Table 5.

Table 5. Chemical composition of purified and regenerated solutions of real electroplating effluents (in mg/L).

Constituent	Initial	Purified		Regenerated
		E = 5 V	E = 10 V	
Sodium	183	103	18	1490
Potassium	3			
Calcium	24			
Magnesium	16			
Ammonia	10.6			
Nitrate + Nitrite	1.6			
Sulphate	1739	998	65	17200
Chloride	210	98	5	220
COD	802			
Nickel	635	424	<1	6430
Iron	1.67			
TDS	4196	1623	89	25340

Energy consumption was 6.4 kW/kg at E = 5 V and 11 kW/kg at E = 10 V. No membrane fouling was observed. These results demonstrated the effectiveness of the electrosorption unit equipped with flat composite membranes for removal of salts from solutions with low salt content, up to 500 mg/L.

The study of electrosorption purification of sulphate solutions with a content of salts up to 3.5 g/L was conducted using a model solution containing: (in mM) 20 Na_2SO_4, 10 NaCl,and (in g/L) 1.15 Na^+, 1.92 SO_4^{2-}, 0.23 Cl^-, and 3.425 TDS. The composition of this solution is similar to sulphate-containing mine waters. The removal of salts from such solutions is of practical importance. The results obtained for the purification of the model solution using an electrosorption module equipped with zirconium phosphate-containing sorption electrodes at E = 5 V and I = 0.15 A are presented in Table 6. The results demonstrated that the flat sheet electrosorption system was highly effective for removal of Ni^{2+} (up to 80 %). Although the nickel-containing solution contained a significant amount of organic matter (COD 802), no fouling of the electrosorption unit was observed. The energy consumption was as low as 6 kW/kg. The flat sheet electrosorption system was also highly effective

Table 6. Purification of modeled mine water solution.

Flow rate, mL/h	Passed volume, mL	Purification degree, %	Energy consumption, kW/kg
200	100	83	5.16
400	150	72	4.06
800	200	50	4.38

for treatment of mine water. For this, the energy consumption was as low as 4 kW/kg.

ELECTROCHEMICALLY-STIMULATED PROCESS ON SORPTION-ACTIVE MEMBRANES

Electrochemically-stimulated process on sorption-active membranes has been applied for the study of desalination of water solutions containing more then 500 mg/L of salts. To increase the effectiveness of the electrochemical reactors, the cathode and anode chambers are usually separated by a membrane. The membrane hampers the movement of ions between the electrodes, decreases their recombination and, therefore, increases the effectiveness of the electrochemical processes. However, the electrochemical sorption reactor also has to include a membrane for separation of the electrode chambers. If that membrane is chemically inert, the directional movement of cations and anions, which are present in the solution, towards the electrodes through the membrane will take place despite obstacles as shown in Fig. 2a. It can be seen that the recombination of H^+ and OH^- ions will take place inside the membrane.

A completely different process is observed if the membrane has amphoteric properties, i.e., it is able to adsorb both cations and anions. In this case, as a result of ion-exchange reactions with cations and anions in solution inside the membrane (this process is described in detail in a previous part of the present paper), additional H^+ and OH^- ions are formed. The increase of concentration of these ions inside the membrane will hamper the movement of other ions, which are electrochemically generated and located in the separated electrode spaces, across the membrane. As shown in Fig. 2b, these ions will be used for neutralization of H^+ and OH^- ions, which are freed as a result of the ion-exchange reaction. Obviously, this process will take place until the membrane sorption capacity is saturated. Then, the membrane becomes chemically inert and the movement of ions can be described by the scheme in Fig. 2a.

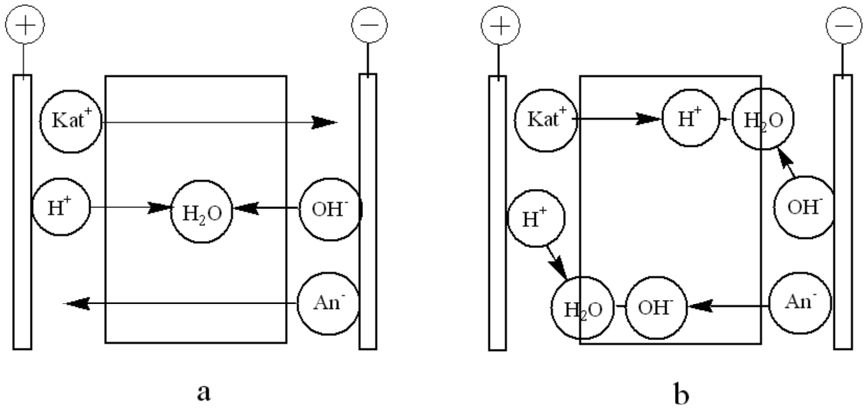

Figure 2. The movement of oppositely charged ions in the electric field in the electrochemical reactor with simple (a) and ion-exchange (b) membranes.

The processes taking place inside the membrane with ion-exchange properties are similar to the processes of electrochemically-activated sorption described in detail in the previous section. This allows elimination of the porous sorption electrodes in the electrochemical-sorption reactor, as long as a membrane is employed as the sorption-active element. This significantly simplifies the construction of the electrochemical reactor and eliminates the necessity to use the electroconductive porous ceramic materials for sorption electrodes and to design reliable current feeders to them. Taking into consideration all the above-mentioned facts, an electrochemical reactor with sorption-active membrane was used to study electrochemically-activated desalination of some water solutions.

The electrochemical reactor used in this study is schematically presented in Fig. 3. The reactor was in the form of a cylinder and its main components were mounted coaxially. The basic element was a metallic cylinder 1. This cylinder was made of titanium and the inside covered with platinum. The tubular ceramic sorption membrane element 3 and rod electrode 4 were fixed inside the reactor with rubber O-rings 2. The titanium rod was covered with platinum. The reactor had two electrode chambers separated from each other 5 and 6. The solutions entered and exited the reactor via the sleeves 7. The electrochemical reactor was a part of the experimental setup shown in Fig. 4.

The initial solution from vessel 1 was fed into the electrode chambers of the electrochemical reactor 4 by peristaltic pumps 2 and 3. The processed solution was collected in vessels 5 and 6. A stabilized power supply device 7 was used. It allowed experiments to be performed using voltage clamp and current clamp modes.

Tubular elements made from porous oxide ceramic (JV «INMA», Ukraine) were used as a basis for preparation of the sorption ceramic elements. The characteristics of the initial ceramic materials were as follows: (i) length 211 mm, (ii) outer diameter 11 mm, (iii) wall thickness 1 mm, content (iv) 70% Al_2O_3 + 30 % ZrO_2, (v) average pore diameter 0.19 µm, and (vi) specific surface area 4.5 - 5.0 m^2/g.

To increase the sorption capacity of porous ceramic materials, dispersed ZrO_2 was incorporated into the pores of the initial material. To implement that, the ceramic material was treated for 1h by a 1M solution of a sol of zirconium hydroxide, as described in the previous section. Then, the ceramic surface was rinsed by distilled water. After that, it was treated by a 25% aqueous solution of phosphoric acid for 1 h and then it was air dried at 200^oC. This resulted in an increase of the internal surface of the ceramic material (from 5 up to 8.5 m^2/g), whereas the pore size was almost unchanged.

A solution modeling mine waters (MMW) was chosen for this research. The composition of this solution is given in Table 7.

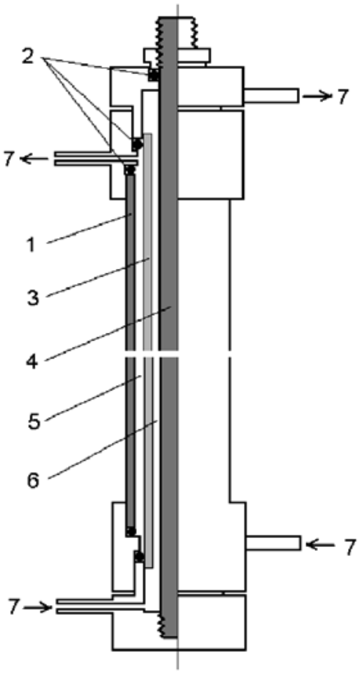

Figure 3. Schematic of the electrochemical reactor for the electrochemically-activated sorption purification of water solutions from ionic contaminants (metal cylinder cover – 1, fixing rubber O-rings – 2, tubular ceramic sorption membrane – 3, rod electrode – 4, electrode chambers - 5 and 6, input and output sleeves - 7).

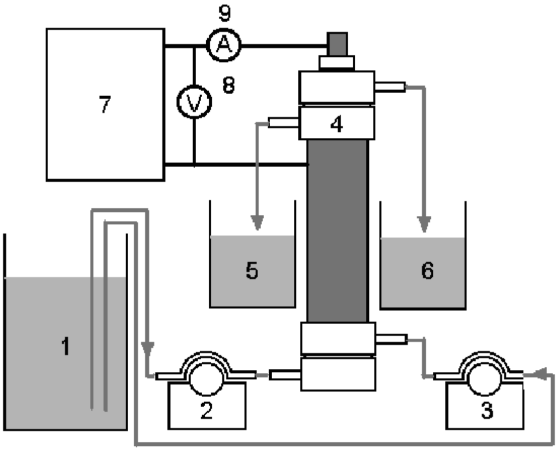

Figure 4. Schematic of the experimental device for the investigation of electrosorption purification of water and water solutions from ionic impurities (vessel for initial solution – 1, peristaltic pumps - 2 and 3, electrochemical reactor – 4, collectors - 5 and 6, stabilized power source – 7, voltmeter – 8, ammeter -9).

Table 7. Composition of the model solution.

Salt	Amount, g/L
NaCl	0.40
Na_2SO_4	2.90
$MgSO_4$	0.75
$CaSO_4$	0.90
TOTAL:	**4.95**

Initially, the sorption activity of standard tubular porous ceramic elements towards different ionic components, which were present in the MMW solution, had been estimated. The main parameter, which was changed in the experiment, was the voltage applied to the electrodes of the electrochemical reactor. The initial solution was fed into both electrode chambers simultaneously. The aliquots of solutions coming from the cathode (catholyte) and anode (anolyte) chambers of reactor were collected. They were analyzed to determine ionic components and pH. The parallel scheme of the solution feeding into the electrode chambers allowed separate assessment of the removal of ionic components by the sorption-active membrane. The rates of solution flow through the electrode chambers were equal at 350 mL per hour. The total volume of solution fed into the electrochemical reactor was 700 mL per hour or 70 volumes per hour, since the reactor volume was 10 mL. This rate of feed is standard for ion-exchange purification systems and widely used for desalination of water solutions (Helfferich 1995). The experimental data obtained is presented in Table 8. The following conclusions can be drawn from comparative analysis of data presented in Table 8. As expected, the removal of cations and anions from solutions, which were fed into the anode and cathode chambers of the electrochemical reactor, respectively is observed. The solution coming from the cathode chamber was alkaline and that coming from anode chamber was acid. Some decrease of the concentration of Ca^{2+} and Mg^{2+} has been observed in solutions, which were fed into the cathode chamber of the electrochemical reactor. This decrease is alleviated by increase of the potential difference between electrodes. The apparent decrease of the concentration of Na^+ and SO_4^{2-} has been observed only in the first portions (up to 100 mL) of the solutions coming from the reactor. The first portions of electrochemically-purified solutions also have an increased degree of removal of Ca^{2+}, Mg^{2+} and Cl^- ions, and this value remains rather significant in the subsequent portions of solutions and increases upon increasing the potential difference between electrodes. The elevation of the potential difference between electrodes results in some increase of degree of purification, amperage of the current, acidity and alkalinity of the output solutions. However, an increase of potential difference higher than 8V is not effective anymore. The results obtained confirm, in general, that the construction of the reactor for electrochemically-activated purification of water from ionic impurities by sorption-active membrane is chosen correctly. The fact that the change of concentration of sodium and sulfate ions is observed only in the first portions of the solutions can be explained by the complete exhaustion of the sorption membrane capacity even during processing the first portions of solutions. The dependence of the degree of removal of these ions on potential difference allows the conclusion that the sorption process is electrochemically activated.

The observed increase of degree of purification of solutions from calcium, magnesium and chlorine ions in the first fractions of solutions, which were electrochemically treated, points to this mechanism also. However, the data in Table 8 show that the main part of calcium, magnesium and chlorine ions is removed according to totally different mechanisms. This fact can be confirmed by the almost constant degree of removal of these ions from all the fractions of the treated solution. A significant dependence of the degree of removal of these ions on voltage is observed. This demonstrates the electrochemical nature of these processes. In fact, the removal of chlorine ions can be observed in the anode chamber according to the reaction:

$$2Cl^- \rightarrow Cl_2 + 2e$$

The following reaction proceeds at the cathode:

$$2H_2O + 2e \rightarrow H_2 + OH^-$$

The removal of calcium and magnesium ions from solution occurs as a result of that reaction. Calcium and magnesium ions interact with OH^- ions according to the following reactions:

Table 8. Purification of MMW solution fed into the electrochemical reactor with sorption-active ceramic membrane modified by hydrated zirconium dioxide.

E, V	V, mL	Anolyte (+)					Catholyte (-)				
		pH	Removal of ions, %				pH	Removal of ions, %			
			Na^+	Ca^{2+} Mg^{2+}	Cl^-	SO_4^{2-}		Na^+	Ca^{2+} Mg^{2+}	Cl^-	SO_4^{2-}
4	0	7.4					7.4				
	50	3.0	70	76	0	0	10.4	0	12	74	65
	100	2.7	50	54	0	0	10.4	0	11	60	45
	150	2.7	20	25	0	0	10.4	0	12	42	17
	200	2.6	3	22	0	0	10.6	0	13	39	0
	250	2.5	0	20	0	0	10.7	0	11	34	0
	300	2.5	0	18	0	0	10.7	0	12	33	0
	350	2.5	0	18	0	0	10.7	0	11	31	0
6	0	8.4					8.4				
	50	2.7	72	79	0	0	11.1	0	3	85	68
	100	2.6	52	60	0	0	11.5	0	4	78	48
	150	2.4	23	55	0	0	11.6	0	5	75	20
	200	2.5	5	45	0	0	11.7	0	3	68	3
	250	2.4	0	42	0	0	11.9	0	4	60	0
	300	2.2	0	40	0	0	11.8	0	6	59	0
	350	2.2	0	40	0	0	11.9	0	5	62	0
8	0	7.9					7.9				
	50	2.6	72	82	0	0	11.6	0	0	87	71
	100	2.5	53	63	0	0	11.5	0	0	84	56
	150	2.5	25	50	0	0	11.6	0	0	83	22
	200	2.5	4	46	0	0	11.6	0	0	80	5
	250	2.4	0	45	0	0	11.7	0	0	80	0
	300	2.4	0	40	0	0	11.7	0	0	81	0
	350	2.3	0	35	0	0	11.8	0	0	78	0
10	0	8.0					8.0				
	50	2.5	70	83	0	0	11.3	0	0	85	72
	100	2.6	55	60	0	0	11.4	0	0	85	52
	150	2.5	22	50	0	0	11.5	0	0	86	18
	200	2.4	3	47	0	0	11.5	0	0	82	3
	250	2.3	0	46	0	0	11.6	0	0	83	0
	300	2.4	0	45	0	0	11.7	0	0	86	0
	350	2.3	0	47	0	0	11.8	0	0	81	0

$$Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2\downarrow$$
$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2\downarrow .$$

These interactions result in the formation, inside the porous membrane, of insoluble (in alkaline media) calcium and magnesium hydroxides. The decrease of concentration of calcium and magnesium ions inside the cathode chamber can also be explained by the formation of the precipitates of these hydroxides. The proposed mechanism can be confirmed by the fact that the degree of purification of this solution from calcium and magnesium ions is up to 80 %, if the solution coming from the cathode chamber is passed through a rather fine filter.

The advantages of modified membranes for the removal of ionic impurities from aqueous solutions are apparent from Table 9. It summarizes data on removal of ionic impurities from MMW solution using the electrochemical reactor with regular inorganic, and modified by zirconium hydroxide, membranes. These data relate to a combined solution. It was prepared by mixing the solutions, which were treated in the cathode and anode chambers, separately. The results presented allow the conclusion that the use of a modified membrane increases the purification degree by more than 50 % and doubles the volume of purified solution. A voltage of 6-8 V and a current of 0.12-0.20 A are optimal for use in the electrochemical reactor used in this study.

Taking into consideration all the experimental data on the use of the electrochemically-activated sorption process for purification of MMW solutions, it is possible to make the following conclusions. Despite the increase of degree of purification, the value is not high enough and it does not exceed 35-45 %. The rather high feed rate of solution into the electrochemical reactor is a possible reason for that. As a result, the contact time of the solution with the sorption-active membrane is short and this did not permit the necessary degree of purification.

To test this assumption, the influence of the quantity of modified sorption-active membrane on degree of purification of MMW solutions has been investigated. For this, a number of electrochemical reactors were used sequentially. The solutions were fed into the cathode and anode chambers of each reactor, separately. The output solutions were mixed after each reactor and fed into the next one. As a result, it was established that the increase of length of sorption-active component does result in a significant increase of degree of purification. The data presented in Fig. 5 demonstrates the increase of degree of purification of MMW solution from sodium ions, if the length of the sorption membrane increases. Fig. 5 shows that the maximum degree of purification (up to 90 %) of the solution (100 mL) can be obtained in reactors with a combined length of the sorption elements of 1 m. It also demonstrates that the value of purification degree decreases, if the amount of solution, passing through the reactor, increases. However, if the volume of the solution increases by four times, the degree of purification decreases less than two-fold. It should also be noted that, if the length of the sorption element is five times longer, the value of electric current doubles. These experiments were conducted at a voltage of 8 V. Analogous dependencies have been found for other ions, which were present in the solution.

The data obtained on degree of purification allows the conclusion that the method of electrochemically-activated sorption is a promising one for the removal of different cation and anion impurities from MMW solution.

Table 9. Comparative data on purification of MMW solution fed into the electrochemical reactor with sorption-active ceramic membrane modified by hydrated zirconium dioxide.

E, V	V, mL	Non-modified membrane				Modified membrane			
		Removal of ions, %				Removal of ions, %			
		Na^+	Ca^{2+}+ Mg^{2+}	Cl^-	SO_4^{2-}	Na^+	Ca^{2+}+ Mg^{2+}	Cl^-	SO_4^{2-}
4	0-100	20	30.5	20	17.5	35	44	37	32.5
	100-200	5	21.5	19	2.5	25	32.5	30	22.5
	200-300	0	17.5	18	0	10	18.5	21	8.5
	300-400	0	19	18.5	0	1.5	17.5	19.5	0
	400-500	0	17.5	18	0	0	15.5	17	0
6	0-100	23.5	32	40	20	36	41	42.5	34
	100-200	6	27	34	5	26	32	39	24
	200-300	0	25	35	0	11.5	30	37.5	10
	300-400	0	24.5	32.5	0	2.5	24	34	1.5
	400-500	0	24.5	30	0	0	23	30	0
8	0-100	23	27	39	21	36	41	43.5	35.5
	100-200	5.5	25	41.5	4	26.5	31.5	42	28
	200-300	0	22.5	40.5	0	12.5	25	41.5	11
	300-400	0	23.5	39.5	0	2	23	40	2.5
	400-500	0	21.5	40	0	0	22.5	40	0
10	0-100	22	31	42.5	21	35	41.5	42.5	36
	100-200	6.5	26.5	42	5	27.5	30	42.5	26
	200-300	0	23.5	43	0	11	25	43	9
	300-400	0	22.5	41.5	0	1.5	23.5	41	1.5
	400-500	0	23	42.5	0	0	23	41.5	0

The main advantage of this method compared to regular sorption processes is the possibility of regeneration of the sorption elements using an electric field without chemical reagents.

The results presented in this section have demonstrated the possibility of applying the electrochemically-stimulated sorption process, which is based on the usage of an active sorption membrane, for removal of ionic impurities from MMW-type solutions. In particular, it has been demonstrated that the application of this method achieves a 90 % decrease of salts content in MMW solutions and produces potable water from solutions containing about 500 mg/L of salts. The effectiveness of this method depends on the type of sorption-active membrane used and it is determined by the value of its

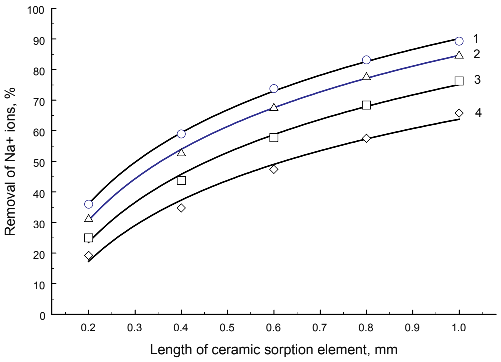

Figure 5. The influence of length of ceramic sorption element modified by zirconium hydroxide on the degree of purification of 100 (1), 200 (2), 300 (3) and 400 (4) mL of MMW solution from sodium ions in the electrochemical reactor.

absorptive capability. The distinct feature of this method is shown by the possibility of non-chemical, almost complete regeneration of the adsorption element by change of the electrode polarities.

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INNOVATIVE WATER PURIFICATION METHOD AND DEVICES

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ABSTRACT

The main sources of drinking water are often polluted by industrial and municipal chemicals. Water treatment plants reduce the concentrations of harmful chemicals in water to a safe level and mandatory disinfection renders water non-hazardous from a bacteriological standpoint. However, conventional water treatment technologies using chlorine result in formation of disinfectant by-products. They have been proved to be strongly carcinogenic. Additionally, water quality deteriorates through the distribution networks. This is due to reproduction and decay of different microorganisms inside the water mains. Thus, at the endpoints of water networks, the concentrations of trihalomethanes, surface-active substances, iron compounds, etc., may exceed the maximum permissible concentration (MPC) by several times, and those of heterotrophs – up to hundred times.

Contaminated water causes at least 80% of human diseases, therefore, innovative technologies for water treatment are urgently needed. There is also a worldwide demand for cost-effective means to prevent consumption of secondary contaminated tap water. Currently, the problem is being solved by manufacturing purified bottled water and by installing adsorption-filtering and osmotic systems. These systems are expensive both to operate and to maintain.

A novel bubble-film extraction system for water treatment is an alternative to the above-mentioned systems. The principle of the innovation is based on the following fact: inherent secondary produced surface-active water contaminants act as water cleaning agents during its treatment by the stream of air bubbles in a space of special geometry. This method has been shown to purify water by 10-100 times more economically than by filtering through

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charcoal. The quality of purified water satisfies the WHO requirements. Pilot scale bubble-film extraction water purifiers were produced and tested. The method can be applied for groundwater conditioning and wastewater post-purification. For advanced purification, very small amounts of special surface-active additives could be used to accelerate adsorption of pollutants to the interface and, hence, increase the degree of water purification. The additive serves as a disinfectant and additional carrier of contaminants such as bacteria, viruses, humic matter, iron and arsenic compounds, etc. The method could be used either in combination with conventional systems or instead of them.

WHAT IS THE PROBLEM?

Surface and ground waters constitute the main sources of drinking water worldwide. These water sources are often polluted by industrial and municipal chemicals. Water treatment plants reduce the concentration of harmful chemicals in water to non-toxic levels and mandatory disinfection renders water non-hazardous from a bacteriological standpoint. However, conventional water treatment technologies using chlorine result in the formation of disinfectant by-products. Chlorine-based organic derivatives have been proved to be strongly carcinogenic. An additional problem arises from water pollution inside the distribution systems. It is due to the reproduction and decay of different microorganisms in water mains. This phenomenon can take place everywhere regardless of the initial water disinfection.

The relationship between the concentration of chloramines (sterilizing agent) and heterotrophic cells, which are the products of secondary tap water bio-pollution, has been studied extensively in the water network in New Jersey (USA) (Woolschlager et al. 2000). It was found that the concentration of chloramines decreases and heterotrophic counts increase significantly as water passes through the distribution system. The average chloramine concentration in the water leaving the treatment plant was about 3 mg/L and it dropped to 0.36 mg/L after 8 kilometers. This loss of chloramine residuals was due to auto-catalytic reactions, in which chloramines spontaneously decay in the bulk water and at the pipe surface, oxidation reactions with reduced forms of organics and iron, and biologically catalyzed reactions, such as reactions with nitrite produced by nitrifiers as well as direct co-methabolism of chloramines by nitrifiers.

At the same time, the heterotrophic counts reached 10^5 cells/mL within the distribution system. The comparison of chloramine and heterotrophs concentrations revealed a very important trend – the concentration of heterotrophs is not strongly related to chloramine concentration. Many areas of the distribution system had bacteria concentration in excess of 10^3 cells/mL in the presence of over 2 mg/L of chloramine. Taking into account that the dry weight of a medium size bacterium is about 4×10^{-9} mg, one can calculate the concentration of heterotrophic cells:

$$C = 4\cdot10^{-9} \times 10^{5} \times10^{3} = 0.4 \text{ mg/L}$$

This concentration is not extremely alarming. However, it could cause significant accumulation of bacterial biomass as biofilm inside the water mains up to 500 mg/m of pipe length per year. Any disturbance of the biofilm inside the pipe initiates the release of organic matter into the transported water. This organic matter interacts with dissolved chlorine forming chloroorganic derivatives. Additionally, organic substances accelerate corrosion of the pipes in the water supplying system increasing the amount of iron and other extrinsic admixtures in the tap water.

The above effects could take place anywhere; however, they are especially strongly manifested inside lengthy water supply networks. The water distribution system existing in Dnepropetrovsk, Ukraine, is a typical example of such a network. In Dnepropetrovsk, the total length of distribution water pipes exceeds 6000 kilometers. Through these pipes, the tap water is supplied to more than one million inhabitants. In summer, there is a water shortage in the town. The deficiency reaches 10^5 m^3 per day. As a result, the water pressure is reduced and water does not reach peripheral districts. In this case, air penetrates into the unfilled water pipes and promotes their destruction due to bio-corrosion and corrosion with oxygen depolarization. The water in the pipes becomes saturated with iron hydroxides and other contaminants. Simultaneously, water undergoes degassing with respect to "active" chlorine. Therefore, the growth of fungi and bacteria accelerates. These processes have an influence on the permanganate water oxidation susceptibility, the concentration of surface-active substances (SAS) and other water quality parameters.

The situation is the same in other big cities. Summarized data on the deviation of water quality from hygienic requirements in Dnepropetrovsk and Kiev is given in Figure 1. It can be seen that water quality must be improved with respect to turbidity, color, permanganate index, concentration of chlorine organic derivatives, SAS, iron and aluminum compounds. Therefore, it is absolutely necessary to post-purify the tap water at the points of its immediate consumption.

HOW IS THE PROBLEM SOLVED AT PRESENT?

There are many methods of water quality improvement. The majority of them are based on water filtration through membranes, carbon adsorption and ion exchange. The commercial devices are manufactured and supplied worldwide by the leading companies, such as Brita, Inno-Water, etc. Both theoretically and practically these systems purify water to an extremely high

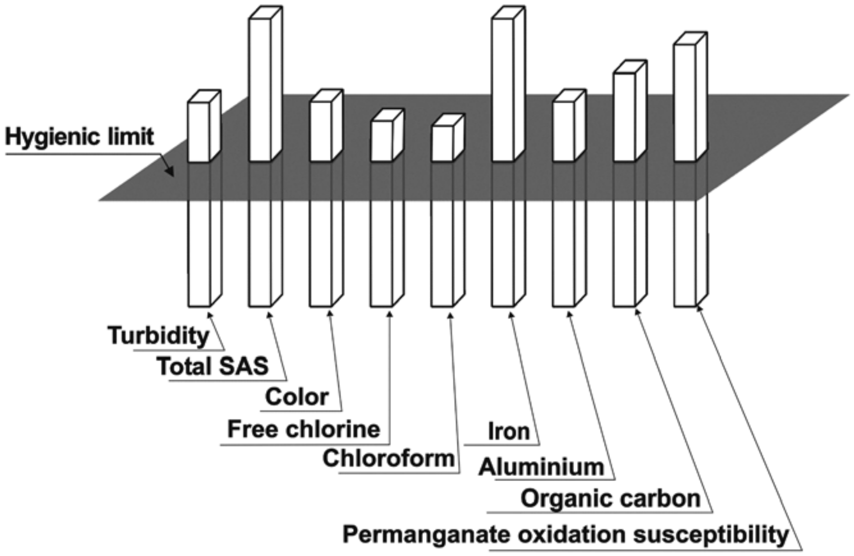

Figure 1. The deviations of tap water quality from hygienic requirements in Dnepropetrovsk and Kiev, Ukraine.

degree. However, some important drawbacks become apparent during their use. In particular, when charcoal or other adsorbents lose their adsorption capacity they also lose the purification ability and become a good substrate for reproduction of different microorganisms. As a result, filtered water becomes more contaminated than entering water. It is also known that ultra-filtration and osmotic membranes cannot serve as efficient barriers to dissolved gases and they are very sensitive to water hardness. Therefore, it is necessary to combine adsorption-filtering and osmotic systems. However, such combinations require regular maintenance and are very expensive in the long run. These disadvantages are critical for Ukraine. Thus, there is a need for new more economical and effective methods of water purification, which are able to give high quality purified water but lack the above-mentioned disadvantages.

WHAT SYSTEM CAN BE CONSIDERED AS AN ALTERNATIVE?

A bubble-film extraction system can be considered as an alternative to the known systems. The bubble-film extraction process is based on the ability of SAS to act as water cleaning agents. The driving force of the purifying process is a stream of air bubbles. This system is very economical and maintains water purification efficiency during use. The bubble-film extraction is similar to flotation in terms of principle of action, but its separation efficiency with respect to SAS removal is about two orders of magnitude higher than that of flotation (Gevod et al. 2002).

The mechanism responsible for the bubble-film extraction is rather simple. Step by step, it is described schematically in Figure 2.

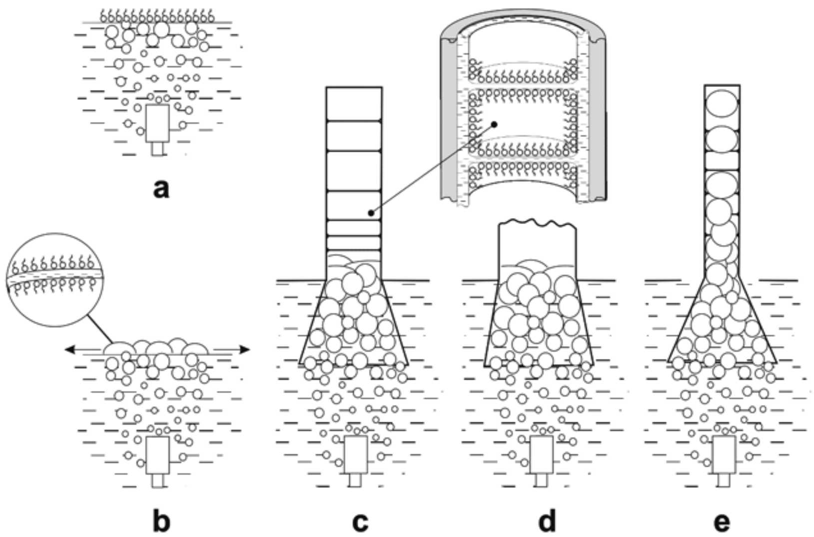

Figure 2. The behavior of air bubbles in air-water system under various experimental conditions.

In particular, Fig. 2a shows the initial stage: air bubbles are produced by appropriate means in the bulk, contaminated water. While passing through the bulk water, these bubbles adsorb surface-active contaminants and deliver them to the planar air-water interface. As a result, the interface becomes filled with an excess of surface-active matter. Subsequently, the air bubbles transferred through the interface saturated with SAS form large hemispherical formations in the shape of half-bubbles. The internal and external surfaces of these formations are covered and stabilized by monolayers of SAS. Herein, the concentration of surface-active contaminants in the liquid body of these formations is much higher than in the bulk water. The structure of half-bubbles is depicted in Figure 2b.

When the above-mentioned formations appear at the air-water interface separated from its surroundings by a pipe with a suitable diameter, the following additional effects occur. First of all, some of the initially formed hemispheres collapse inside the pipe and its interior surface becomes moistened by a solution of SAS. This allows a sliding movement of newly formed half-bubbles upwards along the wetted pipe's surface. This process is accompanied by the transformation of hemispheres into a series of flat thin liquid films (membranes) consisting of a concentrated solution of SAS. Each flat liquid film occupies the cross-section area inside the pipe. Neighboring films are separated from each other by air released from collapsed bubbles. In such a way, a thin liquid film-air dynamic system is formed inside the pipe. It is schematically shown in Figure 2c.

The rate of formation of flat liquid films and their life span until spontaneous collapse are dependent upon the shape and area of the pipe's cross-section, SAS concentration, ionic strength and temperature. A cylindrical pipe with an internal cross-section area in the range 2-4 cm^2 is the most suitable. At larger cross-sections (see Figure 2d), the rate of formation of flat liquid films is sharply decreased. At much smaller cross-sections, the air bubble stream does not form flat films at all. It moves inside the pipe like a continuous gas-liquid mixture as is shown in Figure 2e.

Thus, a pipe of optimum diameter attached to an inverted funnel and installed vertically above the flow of air bubbles is a prototype of the, so-called, bubble-film extractor.

DESIGN AND MODE OF OPERATION OF THE ELEMENTARY BUBBLE-FILM EXTRACTOR

The elementary bubble-film extractor represented in Fig. 3 consists of Π-shaped pipe with conjugation zone of confuser and diffuser. This part of the pipe is connected to an inverted funnel. The device operates as follows. The air bubbles are fed into SAS contaminated water. Passing through the bulk water, they adsorb the molecules of surface-active substances and enter the funnel. This results in the formation of a bubble-liquid column in the bottom part of the device. Inside the column, the rate of vertical motion of each air bubble is sharply reduced compared to their upward movement in the bulk water. The concentration of SAS in the bubble-liquid column is increased as compared to the bulk water, especially at the top of the column. Therefore, when the bubble-liquid column moves through the conjugation zone, it is transformed into a series of thin flat liquid films, as described above. These films consist of concentrated SAS solution and their surfaces are stabilized by monolayers of removed SAS.

Inside the Π-shaped pipe, the films move under the action of pressure released from the collapsed bubbles. The thickness of the films decreases as long as they move towards the exit from the bubble-film extractor. The concentrate of SAS is released from the collapsed films at the output of the device.

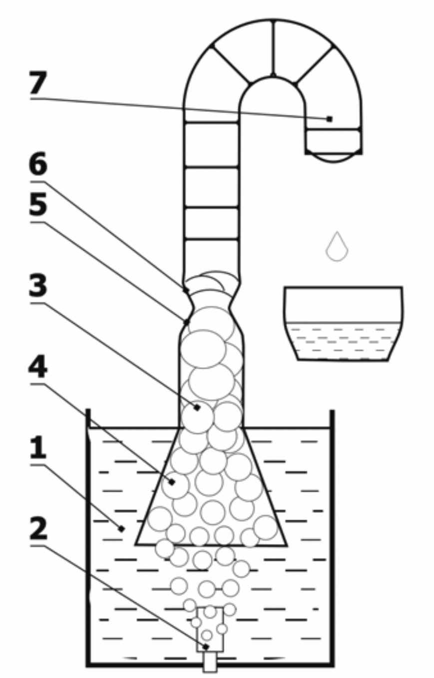

Figure 3. The design of elementary bubble-film extractor: 1 – vessel with treated water, 2 – air sprayer, 3 – internal tube, 4 – entrapping funnel, 5 – confuser, 6 – diffuser, 7 – Π-shaped pipe.

THE RESULTS OF THE TEST OF THE ELEMENTARY BUBBLE-FILM EXTRACTOR

The tests of the elementary bubble-film extractor were carried out using sodium decylsulphate and other detergents such as lipid and protein solutions of various concentrations. Tests of ordinary tap water were also conducted. It was found that the elementary bubble-film extractor allows a reduction of the concentration of various surface-active substances in water by about three orders of magnitude.

The use of the bubble-film extractor is not limited to treatment of solutions of SAS only. The method is also effective in treating aqueous dispersed systems stabilized by SAS, such as polyvinyl acetate emulsion, denatured solution of egg whites, dispersion of hydrolysed aluminium sulphate in the presence of anionic SAS, and other colloid systems. Perfect separation was observed in all cases studied (Gevod et al. 2002).

In general, the post-purification process by means of bubble-film extraction could be schematically described as follows:

Bulk water with SAS and other contaminants
↓
Air bubbles are fed into contaminated water
↓
Surface-active and complementary contaminants are adsorbed on uprising air bubbles
↓
Bubbles with adsorbed contaminants are transformed into thin liquid films flowing inside the bubble-film extractor
↓
Pollution is removed through the bubble-film extractor in the form of a thin liquid film flow.

The bubble-film extraction has an important advantage as compared to regular flotation, microflotation, ionic flotation, and foam separation. During the bubble-film extraction, a special channel isolates the stream of floated products from the water surface. Thus, the adsorbate is completely transferred into thin liquid films, and does not dissolve back into the aerated water. This results in very high efficiency of the bubble-film extraction. For example, the concentration of targeted contaminants could be decreased to the limit of their analytical determination. The concentration profiles of different contaminated waters in air bubble–water systems vs. time of the bubble-film extraction process are presented in Fig. 4.

Experiments conducted in our laboratory have shown that the bubble-film extraction is able to improve tap water quality with respect to a number of parameters. The results of these experiments are summarized in Table 1.

The experimental details were as follow. The treated volume of water was 3 liters. The air-sprayer was placed 10 cm below the capturing funnel. The rate of the air discharge for bubbling was about 1 L/min. The water samples were treated for 20 minutes. The chemical and microbiological analyses were carried out in accordance with standard methods.

Comparison of the results obtained with hygiene standards shows that bubble-film extraction improves water quality with respect to all tested parameters. The advantage of this method becomes especially obvious if the low energy consumption required running the bubble-film extractor is considered. Typically, the power consumption does not exceed 1 W×h per liter of treated water.

It is worth noting that the efficiency of bubble-film water purification is directly proportional to the degree of water pollution by endogenous SAS. Their concentration in the tap water of big cities is usually sufficient for

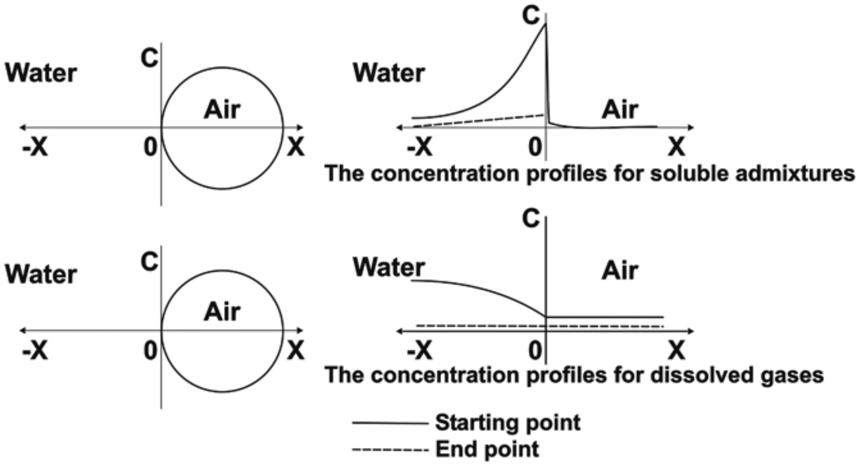

Figure 4. The concentration profiles of different contaminated waters in air bubble – water systems vs. time of bubble-film extraction.

Table 1. The efficiency of water treatment by bubble-film extractor.

Parameter	Initial water	Treated water	Standard
Colouration, degree	20 – 50	< 20	20
Odour, points	2 – 3	1	2
Turbidity, mg/L	4 – 14	0.87 – 3	1.5
pH	7.25 ± 0.3	7.32 ± 0.1	6.0 ÷ 9.0
Taste and aftertaste, points	2 – 3	1	2
Residual chlorine, mg/L	1.2	< 0.6	0.8÷1.2
Chloroform, mg/L	0.1	Unfound	0.06
Tetrachloride, mg/L	0.004 – 0.006	Unfound	0.005
Aluminium, mg/L	0.24±0.02	0.11 ± 0.001	0.5
Iron, mg/L	3.0 – 14.0	2.0 – 11.0	0.3
Cadmium, mg/L	0.0005	Unfound	0.001
Strontium, mg/L	0.103	0.09	2.0
Ammonia, mg/L	< 0.04	Unfound	2.0
SAS, mg/L	3.0	<0.025	1.0
SAS, mg/L*	0.5	<0.04	0
Arsenic, mg/L	0.005±0.0001	Unfound	0.05
TMA (per 1 mL) *	63–630	27 – 150	100
Coli-index*	100000	50000	< 3

* Loading experiment.

effective water quality improvement. If water does not contain a sufficient amount of endogenous surface-active contaminants, it is necessary to inject into the water some surface-active reagent. This increases the degree of removal of various «target» contaminants from treated water.

This innovative approach is currently under investigation in our laboratory. So far, it has been found that a small amount of special surface-active chemical added to the treated water accelerates adsorption of contaminants and, hence, increases the degree of water purification by bubble-film extraction. This additive acts as a disinfectant, additional collector and carrier of «target» contaminants, such as bacteria, viruses, humic matter, iron and arsenic compounds, etc. This innovation increases the efficiency of bubble-film extraction. Water is treated more effectively in a single unit and in one step.

WATER PURIFIERS BASED ON BUBBLE-FILM EXTRACTION

A number of novel water purifiers based on bubble-film extraction were designed in our laboratory and manufactured. These devices are intended for personal and communal use. Three very economical and convenient devices for personal use are shown in Fig. 5. Fig. 5*a* shows the water purifier for post-purification of secondary polluted tap water with an output rate of about 1.5 L/hour. This device consists of three main parts: the purifying module (I), the vessel for purified water (II), and an air pump with a flexible pipe (III). The purifying module comprises a bubble-film extractor connected to a funnel and a collector of wastes with a removable cover made of plastic used for foodstuffs. This water purifier is installed on the top of a special reservoir filled with water. The purification process begins from the moment the air pump is turned on.

At the beginning of operation, the initial concentration of surface-active and other contaminants in the bulk water is large. The bubbles flowing inside the bubble-film extractor form the bubble-liquid column, which is transformed into the liquid films at the upper part of bubble-film extractor. This column moves upwards inside the pipe (stem of the funnel) and breaks down at the upper opening of the pipe, releasing wastes into the waste collector. The intensity of generation of the liquid film is reduced as the concentration of SAS is decreased. When water does not contain SAS the thin flat liquid films of concentrated contaminants are not formed inside the bubble-film extractor. To complete water decontamination, it is necessary to achieve a ratio of treated water volume to total air bubble volume not less than 1:40. Therefore, the treatment lasts for about two hours for 3 L of water and air pump capacity of 1 L/min of compressed air.

Water purifiers shown in Fig. 5 *b* and *c* are equipped with the same purifying module, but, in the device *b*, the air bubble stream is produced by a special impeller, which is driven by an electric motor consuming about 2 W×h of power. In the device *c*, the air stream is generated by a special injector. This device allows post-purification of 3-50 L of water, depending on the type

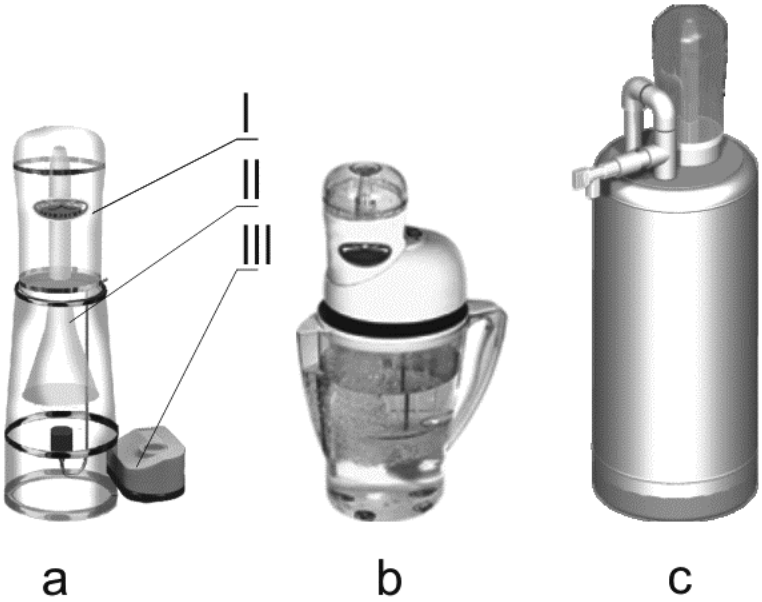

Figure 5. The assortment of the bubble-film water purifiers.

of vessel used. In this device a submersible pump consuming 12-15 W×h is used.

A more complex and powerful water purifier is represented in Figure 6. This is a flowing bubble-film water purifier and it is capable of producing up to 3 m^3 of purified water per day. In this device, water is treated under stationary conditions with a flow rate of about 2 L/min. The volume of collected wastewater does not exceed 3% of treated water. Compressed air is created by a membrane air pump producing about 140 L/min of air at a pressure of 0.35 MPa. The air discharge in each column is 35 L/min.

SUMMARY

The bubble-film extraction method and bubble-film water purifiers are mainly designed for tap water post-purification as an alternative to existing systems. In contrast to the osmotic and adsorption-filtering devices, the bubble-film water purifiers do not require any replacement parts. During the bubble-film extraction, the air bubbles fed into water adsorb the surface-active substances together with other surface-inactive compounds. Subsequently, the bubble flow is transformed into a flow of thin flat liquid films (membranes). Each membrane consists of a concentrated solution of water contaminants. The amount of adsorbate, Q, inside each film is described by the equation:

Figure 6. Flowing bubble-film water purifier with productivity up to 3 m^3 of purified water per day.

$$Q = 4\pi r^2 kCn\tau$$

Here, r is the radius of an air bubble, k is the rate constant of adsorption of water contaminants at the air bubble surface, C is the bulk concentration of contaminants, n is the number of air bubbles forming one liquid film, τ is the residence time of an air bubble in the bulk water.

The rate of bubble-film water purification is directly proportional to the concentration of SAS, intensity of bubbling, and the length of air bubble pathway in the bulk water. Thus, optimisation of the process is possible by changing the bubbling intensity, the length of the air bubble pathway and by increasing the number of removing channels in the bubble-film extractor at given water flow. Doing so, it is easy to achieve the required degree of water purification at minimal power and material consumption.

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POTENTIALITIES OF MEMBRANE OPERATIONS IN WATER TREATMENTS

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INTRODUCTION

The problem of water scarcity, once typical for arid areas such as Arabia or Africa, is now becoming a common issue all over the world. The continuous increase of industrial activities and climate changes due to greenhouse phenomena are among the causes of this problem. To continue "the run towards technology", while preserving natural sources, it is necessary to develop new systems of production capable to work more efficiently than previous ones and in harmony with the environment. Following this logic, the objective of the present study is to describe how the implementation of membrane units into industrial cycles could improve the existing processes. In particular, the performance of nanofiltration, reverse osmosis and membrane contactor units, both as single devices and in integrated schemes, is analyzed for the sparkling water process, production of mineral water with controlled composition, water desalination, and water purification at oil refineries. The proposed flowsheets and the traditional ones are compared in terms of efficiency, costs, energy consumption and environmental impact.

MEMBRANE CONTACTORS IN THE SPARKLING WATER PROCESS

Membrane contactor (MC) represents a new membrane system used to perform mass transfer between phases (Rangwala 1996, Bhaumik et al. 1998, Vladisavljevic 1999, Gabelman and Hwang 1999, Leiknes and Semmens 2001). The membranes are microporous, not selective, and have the function of keeping the phases involved in contact. The membrane material is often

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Modern Tools and Methods of Water Treatment for Improving Living Standards, 151–158.

hydrophobic polypropylene. If an aqueous phase is present, it cannot penetrate through the micropores and the interface is established at the pore mouth (Fig. 1). If both phases are aqueous, then a gaseous gap is created in the membrane pore through which all volatile species (including water vapor) can be transferred (Fig. 2).

Figure 1. Hydrophobic microporous membrane section and phase distribution for (a) liquid-liquid and (b) gas-liquid applications.

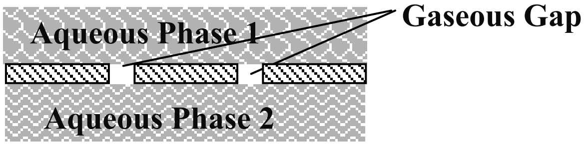

Figure 2. Hydrophobic microporous membrane section and phase distribution for aqueous-aqueous solutions applications.

In sparkling water production, the water is first deoxygenated in a stripping column using CO_2 as a stripping gas and subsequently carbonated by injecting CO_2 under pressure in a second column (saturation step). With membrane contactors, it is possible to combine the above two steps in a single unit by feeding the water from one side of the membrane, while flowing the CO_2 stream from another side (Fig. 3). Due to difference in partial pressures, the oxygen leaves the water phase towards the CO_2 stream and the CO_2 is added into the liquid (Fig. 4). Several experiments have been carried out in a commercial module and a mathematical model has also been developed to analyze the performance of this system (Criscuoli et al. 2003). During the experiments, the effect of many parameters (temperature, pressure, oxygen concentration, etc.) on the efficiency of the operation has been evaluated. Interestingly, the liquid phase offers a higher mass transfer resistance with respect to the gas phase. The rate of oxygen removal increases upon increasing the liquid flow rate (Fig. 5), whereas no variations were observed if the gaseous flow rate was changed.

The system is able to handle significant changes of the inlet oxygen concentration ranging from 0.9 up to 9 ppm keeping the oxygen removal rate relatively constant. Comparison between membrane contactors and the traditional equipments is reported in Table 1.

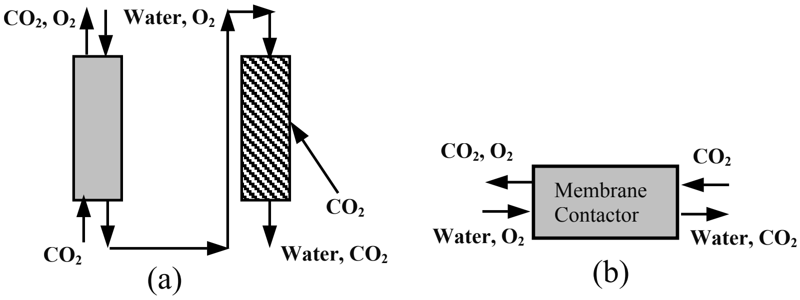

Figure 3. Sparkling water production by traditional system (a) and membrane contactor (b).

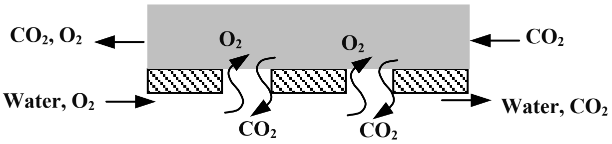

Figure 4. Simultaneous transfer of oxygen and carbon dioxide in a membrane contactor.

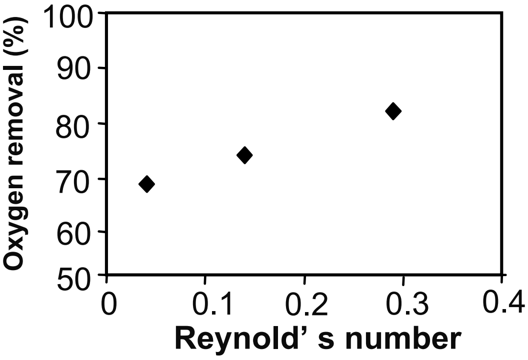

Figure 5. Effect of Reynolds number (water flow rate) on the oxygen removal.

Membrane contactors have lower capital cost, lower CO_2 consumption, and are substantially smaller in size than the stripper-saturator system. The environmental impact, calculated as CO_2 released into the atmosphere, is the same. Head-to-head comparison of the membrane contractor and the stripper- saturator system shows that the former has higher operational cost due to the membrane replacement (25,900 Euro/y),

Table 1. Comparison between traditional and proposed systems.

Parameter	Traditional/Proposed
Equipment cost (Euro)	2.24
CO_2 consumption (kg/h)	1.73
CO_2 cost (Euro/h)	1.73
CO_2 in the atmosphere (kg/h)	1
Membrane replacement (Euro/y)	NA
Volume (m^3)	12

however, significant reduction of this value is expected once large-scale production occurs, which will further increase the competitiveness of membrane contactors.

PRODUCTION OF WATER WITH CONTROLLED COMPOSITION USING INTEGRATED MEMBRANE SYSTEMS

The production of drinking water with the desired ionic composition is becoming an important target for beverage companies in order to satisfy both more stringent regulations and customer needs. Membrane-based devices, with their intrinsic flexibility, might be suitable for reaching this goal. For example, nanofiltration (NF) and reverse osmosis (RO) units utilized separately or as parts of integrated systems, can be used. Currently, the potentialities of these membrane systems in achieving the desired final water compositions from ”mother water” are being investigated at the Institute on Membrane Technology (ITM, Italy). For this purpose, different systems have been considered and Table 2 shows the relative results. If “mother water” is processed by reverse osmosis only, the water obtained at the permeate side is characterized by a low content of all ions. Diversity in ionic composition can be achieved by coupling the nanofiltration to reverse osmosis. Both schemes, RO-NF and NF-RO, with a certain recycle-ratio have been analyzed (Fig. 6 and 7). It can be seen, that the streams at the outlets of two systems differ in composition. On this basis, any type of water composition can be obtained. For example, final water with high content of calcium ions and low amount of sodium can be produced by mixing the exiting streams: NF permeate with RO retentate in scheme 1 or RO permeate with RO retentate in scheme 2 (Table 3).

By varying the recycle-ratio, different results can be obtained; furthermore, other types of combinations are also possible. Thus, integration of the membrane units allows the production of a final water composition depending on the desired target.

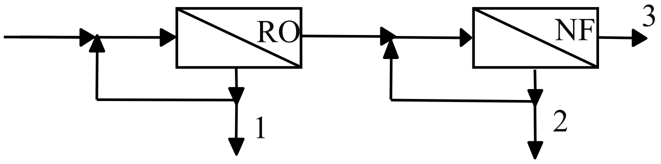

Figure 6. RO-NF scheme (scheme 1).

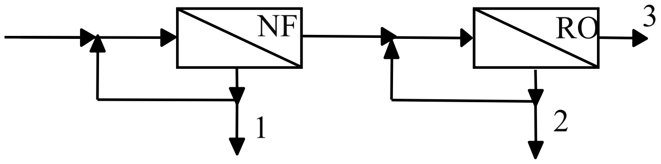

Figure 7. NF-RO scheme (scheme 2).

Table 2. Water composition (mg/L).

	Feed	Scheme 1			Scheme 2		
		1	2	3	1	2	3
Ca	72.4	196	3.37	1.41	64.4	252.46	3.54
Mg	14.3	39	0.81	0.25	12.86	49.88	0.70
Na	17	43.5	11.39	0.26	57.22	16.38	1.16
K	3	7.55	2.32	0.08	8.92	3.73	0.34
SO_4	46	126	0.79	0.16	166	41	0.10

Table 3. Water composition (mg/L).

	Scheme 1	Scheme 2
	Mix of 3 and part of 1	Mix of 3 and part of 2
Ca	10	20
Mg	1.86	3.9
Na	2	2
K	0.39	0.56
SO_4	5.4	2.75

INTEGRATED MEMBRANE SYSTEMS IN WATER DESALINATION

Water desalination by reverse osmosis is a well-established process for recovery of freshwater from brackish water and seawater. The freshwater recovery factor, energy consumption, environmental pollution and brine disposal are some important related issues. The performance of reverse osmosis can be significantly improved by coupling different membrane units to the reverse osmosis unit. Microfiltration (MF), ultrafiltration (UF), and nanofiltration operating prior to the reverse osmosis stage have already been introduced in the desalination flowsheet (pre-treatment step) in order to reduce fouling phenomena and to increase freshwater production. During the process, the control of the water-gas composition is an important issue due to the following:

- dissolved oxygen and carbon dioxide might be responsible for the corrosion problems affecting the material life of the plant;
- pH and conductivity of water are dependant on the CO_2 content;
- when water disinfection (e.g., water ozonation) is necessary, adequate control of the amount of the disinfecting gas has to be achieved;

gases such as H_2S contained in the water have to be totally removed.

Usually, the gas removal is carried out in the stripping columns and the final pH is adjusted using NaOH. In order to avoid the use of chemicals and to better control the content of the various gases, membrane contactor units can be utilized either for removal or for injection of gases. Membrane contactors can also improve the efficiency of reverse osmosis of the brine (so-called, membrane distillation). The brine disposal represents, in fact, one of the most critical steps of the entire operation, taking into consideration both economical, which includes construction of pipelines and disposal points, and environmental aspects. It is possible to further concentrate the brine after the reverse osmosis using membrane distillation, which leads to an increase of freshwater production and to a substantial reduction of brine produced. Moreover, by concentrating the brine up to saturation, valuable salt can be crystallized, and the brine disposal problem might be totally eliminated (Drioli et al. 2002). An analysis of the performance of the integrated NF/RO/MC system has been attempted by Criscuoli and Drioli (1999). In particular, a comparison between the desalination schemes usually employed (NF/RO) and the proposed one has been made in terms of energy consumption, water recovery, and brine production (Table 4). As a result, the weak point of the system seems to be the higher energy consumption related to the membrane distillation unit; this value can decrease if thermal energy is available in the plant. Concerning the use of membrane contactors for the control of the water gas composition, there is no increase of energy consumption because the operation is carried out at atmospheric pressure; furthermore, the use of chemicals is avoided.

Table 4. Comparison between NF/RO and NF/RO/MC integrated schemes.

	NF/RO	NF/RO/MC
Water recovery (%)	45	80
Brine production (m^3/h)	572	212
Energy consumption (kWh/m^3)	4.53	13

MEMBRANE CONTACTORS FOR WATER PURIFICATION IN THE PETROCHEMICAL INDUSTRY

Conventionally, in the ethylene production cycle, gases coming from cracking furnaces are cleaned using large quantities of steam in stripping towers. Processed water is then purified in order to re-use it in the system. A study on the possibility to apply membrane contactors for the water purification step has been performed (Bernardo et al. 2003). Fig. 8 demonstrates the scheme used for the analysis. Two stripping phases have been considered: air and ethane (available at the plant).

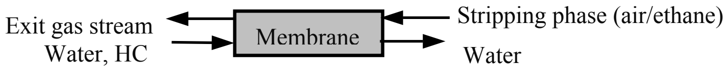

Figure 8. Hydrocarbons removal from aqueous streams by membrane contactors.

Table 5 shows a comparison between the traditional process (stripping towers) and the membrane contactor.

Table 5. Comparison between stripping towers and membrane contactors.

	Stripping towers	Membrane contactors
Strip phase	Steam	Air/ethane
Removal (%)	90	90 (35°C)–99 (70°C)

It can be seen that membrane contactors allow higher hydrocarbons removal and avoid the use of high quantities of steam. Furthermore, membrane contactors are smaller compared to conventional units.

CONCLUSIONS

Existing water treatment operations can be effectively improved by employing membrane technology. The reduction of equipment size, higher efficiency, and lessening of environmental impact are all important achievements that could be reached by the implementation of membrane systems. Their flexibility and modularity permit easy integration into traditional cycles of production, which leads to enhanced performance of the processes and enhances the possibility of sustainable development.

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WATER DISINFECTION USING SILVER AND COPPER IONS AND COLLOIDAL GOLD

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ABSTRACT

The efficacy of using Ag^+ and Cu^{2+} metal ions and colloidal Au combinations (within the limits of current drinking water regulations) for killing *Typhoid-Paratyphoid, Legionella pneumophila*, *Salmonella*, *Vibrio cholerae asiaticea*, *Lamblia intestinalis, Cryptosporidium parvum, etc.* has been examined. Tests carried out in various laboratories during 1998-2003 have shown the dependence of bacteria killing time on metal ion concentration, initial bacteria concentration, and the influence of the concentration of various ions (Cl^-, SO_4^{2-}, S^{2-}, Fe^{2+}, Fe^{3+}) on the disinfection process.

INTRODUCTION

At present, the development of effective and affordable methods of water disinfection is an important task especially in the regions, where freshwater resources are limited and unevenly distributed and drinking water often contains extraordinarily large amounts of pathogenic bacteria.

The water disinfection method described here represents an improvement of existing methods based on the destructive impact of low concentrations of metal ions on bacteria in water. During the disinfection, the alloyed electrodes, placed into the water, release metal ions under the influence of a corresponding current. The released metal ions bind to the bacterial cell wall causing its disruption and lysing. Various metals are used as the electrode materials, for example, silver (Kulsky 1982), copper, and an alloy containing silver and copper in different proportions ranging generally from 10/90 to 30/70 (Landeen 1989, The Silver Institute 1999).

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The concentration of electrolytically introduced metals in the disinfected water is of significant concern, particularly for potable applications. The maximum concentrations of metals in drinking water are regulated at various levels in different countries. For example, copper is regulated in the United States at a concentration of 1.3 mg/L (which is an *action level*, not a maximum contaminant level); silver is regulated at a concentration of 0.1 mg/L as a secondary (*i.e.,* non-enforceable) constituent because of its aesthetic effect; the discoloration of plumbing fixtures. The drinking water regulation limit in the Commonwealth of Independent States is 0.1 mg/L for Cu and 0.05 mg/L for Ag, respectively. The concentration of metal ions required for disinfection is sometimes greater than the regulatory limits and, as a result, the method cannot be used.

The purpose of this work was to create a new water disinfection device with low energy consumption, which consists of alloy electrodes releasing effective levels of metal ions lower than the regulations specified above.

MATERIALS AND METHODS

Electrodes made of Ag-Cu-Au alloy with various compositions (Ag from 39 to 100%, Cu from 0 to 60%, Au from 0 to 0.2%) were tested. The test water from the container 1 (Fig. 1) was re-circulated by pump 2 through the test apparatus.

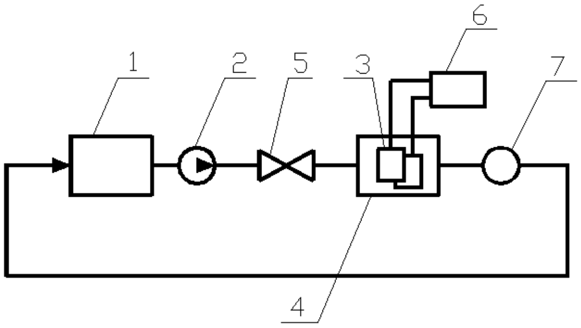

Figure1. Schematic diagram of the experimental apparatus: 1 - container with test water, 2 - pump, 3 - electrodes, 4 - pipe, 5 - valve, 6 – direct current generator, 7 - flow meter.

The electrodes had various shapes: (i) a ball with diameter 5 mm, (ii) a disc with diameter 20 mm, and (iii) a rectangle 20 mm x 30 mm. The alloy electrodes 3 were placed into the water pipe 4 and a current was applied to the electrode to cause the release of Ag and Cu as ions, and Au as a colloid. The distance between electrodes was varied from 8 mm to 20 mm. A control valve

5 regulated the water flow rate between the electrodes. A direct current generator 6 supplied a stable electric current between the electrodes, independent of the water conductivity. A flow meter 7 regulated the water flow rate between the electrodes to provide electrochemical release of the necessary amount of metals.

Experiments were conducted with the following bacterial cultures: *Escherichia coli* (272), (Strain 33218), (NCTC 10538), fecal coliforms, *Salmonella typhimurium* (251), *Salmonella typhi* (495), *Salmonella paratyphi* (8138), *Legionella pneumophila* serogroup 1, and *Vibrio cholerae asiaticea* (157) at a temperature ranging from 18-36°C. The cultivation, culture enrichment and testing of the bacteria were performed following the standard testing methods (Drinking Water 1982) for the evaluation of disinfection, which are analogous to Standard Methods for the Examination of Water and Wastewater (American Public Health Association 1995).

A bench-top pH Meter (Cole-Parmer) and ion-selective electrodes (Cole-Parmer) were used to determine the concentrations of Ag^+ and Cu^{2+} (for $[Cu^{2+}] > 0.05$ mg/L). Lower concentrations of Cu^{2+} and Au were determined by neutron-activation analysis. For this, water samples were irradiated using the nuclear reactor at the Institute of Nuclear Physics (Tashkent, Uzbekistan). A Ge(Li) detector with a resolution of about 1.9 keV at 1.33 MeV and a 6144-channel analyzer were used. The areas under the γ-peaks of the radionuclides ^{64}Cu (half-life of 12.8 h, energy of the γ-peak 0.51 MeV) and ^{198}Au (half-life of 64.8 h, energy of the γ-peak 0.41 MeV) were measured to calculate the concentrations of Cu and Au, respectively. The sensitivities of determination of Cu and Au (irradiation in a reactor with a neutron flux of $1x10^{13}$ neutrons/cm^2 s) were 10^{-9} g/g and 10^{-10} g/g, respectively, with a standard deviation within 10% (Alfassi 1990).

Two types of device were used in the experiments. The first one was a portable experimental water disinfection device that consisted of a 12V battery, a direct current generator and electrodes made of an alloy containing 79.9 % Ag, 20% Cu, and 0.1% Au (Khaydarov et al. 1997, 2001). The second device, designated for field experiments, was attached to the nozzles of manual water pumps employed for pumping well water. The average delivery capacity of the pumps was 1 m^3/h and the instantaneous peak value of the water flow rate was 3.6 m^3/h. The actual disinfection device consisted of a solar 12V battery connected to an accumulator, an electronic unit and electrodes made of an alloy containing 79.9 % Ag, 20% Cu, and 0.1% Au. The electric current between the electrodes was automatically flow-regulated by the water flow meter (see equation 3 below). The energy consumption of the devices was 0.5 Wh.

Additionally, independent tests of the first experimental device were performed at the Department of Pathology of the University Sains Malaysia in 1999. Pond water samples (5L) were each contaminated with 5 g of faecal matter. The initial bacteriological quality was estimated at 5 x 10^{12} CFU/L coliforms. The insertion time, i.e., the water treatment time by the device at the specifically set electric current, was 30 minutes and the concentrations of Ag^+, Cu^{2+} and Au were 0.5 mg/L, 0.12 mg/L and 1.2 μg/L, respectively. Samples were analyzed 1 h, 3 h, 1 day, and 1 week post-treatment.

RESULTS AND DISCUSSION

The amount of bacteria killed during the disinfecting time t is proportional to the amount N of all bacteria and the effective concentration C of metal ions in water and inversely proportional to the coefficient K of resistance. The coefficient of resistance depends on bacteria type and the concentrations of cations and anions that can react with the disinfecting metal ions.

$$\frac{dN}{dt} = -\frac{C}{KN} \qquad (1)$$

From (1), one can obtain:

$$N_F = N_0 \exp(-\frac{Ct}{K}) \text{ or } Ct = K \ln(\frac{N_0}{N_F}) \qquad (2)$$

where N_o and N_F are the initial and final concentration of bacteria, respectively, t is the disinfection time. The above shows that the concentration of metal ions C and time t necessary for water disinfection depends logarithmically on the initial concentration of bacteria, N_o.

Experimental results presented in Table 1 demonstrate the synergistic disinfection effects obtained by using electrodes made of alloys with various silver/copper/gold combinations. The estimation of the technical characteristics of the devices, which are needed to achieve the most effective concentrations of disinfection ions in the water, can be carried out by using the concentration of Ag^+ as a reference ion. Table 1 shows that the best disinfection effect is obtained by using an alloy containing 70-90 % Ag, 10-30 % Cu and 0.1-0.2 % Au. Employing electrodes with such a composition allows minimization of K, and considerably reduces the metal ion concentrations in the water as compared to other combinations. For such electrodes, the data on the coefficients K for various pathogens and disinfection times are summarized in Table 2. The most effective concentrations of silver, copper and gold in treated water were 30 μg/L, 7.5 μg/L and 0.075 μg/L, respectively, which are all less than current drinking water regulation limits.

Table 1. Minimum concentration of disinfecting metal ions for killing *E. coli* with an initial concentration of 1000 CFU /L (down to a final concentration ≤ 1 CFU/L) within 30 minutes.

Composition of electrodes, %			Concentration of Ag^+, mg/L	K, mg×s/L
Ag	Cu	Au		
100.0	0.0	0.0	1.5	390 ± 120
99.9	0.0	0.1	1.5	390 ± 120
99.8	0.0	0.2	1.5	390 ± 120
90.0	10.0	0.0	0.1	26 ± 8
89.9	10.0	0.1	0.05	13 ± 4
89.8	10.0	0.2	0.05	13 ± 4
80.0	20.0	0.0	0.05	13 ± 4
79.9	20.0	0.1	0.03	8 ± 3
79.8	20.0	0.2	0.03	8 ± 3
70.0	30.0	0.0	0.05	13 ± 4
69.9	30.0	0.1	0.04	10 ± 3
69.8	30.0	0.2	0.04	10 ± 3
50.0	50.0	0.0	0.5	130 ± 40
49.9	50.0	0.1	0.3	80 ± 25
49.8	50.0	0.2	0.3	80 ± 25
40.0	60.0	0.0	1.0	261 ± 80
39.9	60.0	0.1	0.8	210 ± 60
39.8	60.0	0.2	0.8	210 ± 60

Table 2. Disinfection time for various bacteria types in the water after electrochemical release of silver, copper and gold at 30 µg/L, 7.5 µg/L and 0.075 µg/L, respectively (N_o=1000 CFU/L).

Pathogen	K, mg×s/L	t, min
Typhoid – Paratyphoid, *Legionella pneumophila*	15 – 30	60
Salmonella	8 – 15	30
V. cholera	8 – 15	30

The influence of various cations and anions (*e.g.,* Cl^-, SO_4^{2-}, S^{2-}, Fe^{2+}, Fe^{3+}) in the water on the disinfection process was investigated. For this, NaCl, Na_2SO_4, Na_2S, $Fe(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ were added to obtain the necessary water solutions. The results of tests using the electrodes with the optimal composition described above are given in Table 3. The initial concentration of *E. coli* in these experiments was 10^7 CFU/L, and the concentration of Ag^+ ions in the water was 0.1 mg/L (the corresponding concentrations of Cu^{2+} and gold were 25 µg/L and 0.25 µg/L, respectively). These results show that only Cl^- and Fe^{2+} react with the disinfecting metal ions and increase the disinfection time (*i.e.,* increase the coefficient K) due to formation of AgCl and reduction of ions by Fe^{2+}.

Table 3. Influence of cations and anions on disinfection time of *E. coli* (initial concentration 10^7 CFU/L).

Ion	Concentration of ions, mg/L	Time after water treatment					
		15 min	30 min	60 min	90 min	2 h	24 h
Cl^-	2	300	3	<1	<1	<1	
	6	1200	23	3	<1	<1	
	20	2400	220	4	<1	<1	
	60	5000	2800	170	10	<1	
	350	10^4	5000	890	70	12	<1
SO_4^{2-}	1.5		230	<1	<1		
	25		290	<1	<1		
	250		250	<1	<1		
S^{2-}	0.01	1000	120	<1	<1		
	0.05	1200	120	<1	<1		
	0.15	1600	140	<1	<1		
	0.30	1800	150	<1	<1		
Fe^{2+}	1.5	5700	2700	1600			
	15	10^4	7900	3800			
Fe^{3+}	1.2	2000	40	20	<1		
	11.1	2200	110	9	<1		

The portable experimental device with the electrode made of the alloy described above has been tested by the Ministry of Defence of Uzbekistan and the University Sains Malaysia. In those trials, the dependence of disinfection time on the effective concentration C, initial bacteria concentration N_o (from 10^3 to 10^{12} CFU/L), and organism type has been investigated. In the Central Sanitary and Epidemiological Laboratory of the Ministry of Defence of Uzbekistan, this device was tested using two contaminated water samples containing 10^8 and 10^9 CFU/L *E. coli*. The electric current between the electrodes was set at 5 mA. The electrode insertion times were 3, 5, and 10 min, which correspond to concentrations of Ag^+ and Cu^{2+} of 50 and 12.5 µg/L, 80 and 20 µg/L, and 160 and 40 µg/L, respectively. This allows use of the described method for wastewater treatment or for drinking water disinfection in emergency cases. The efficiency of disinfection was evaluated, in these trials, over a 20-day period following disinfection, to determine the rate of bacterial re-growth. Some results are presented in Table 4.

It should be noted that the insertion time in these experiments was greater than that obtained in laboratory tests. This is due to the fact that natural water typically contains chloride-ions Cl^-. During the electrolytic process, the local concentration of Ag^+ in the thin water layer near the surface of the anode increases considerably, so insoluble AgCl is formed (solubility product 1.8×10^{-10}) controlling the concentration of Ag^+ at low levels. Similarly, metal hydroxides (*e.g.* $Cu(OH)_2$) are formed near the cathode. Thus, the concentrations of metal ions (Ag^+, Cu^{2+}) are lower than those calculated from Faraday's laws of electrolysis.

Table 4. Test results of the portable experimental device with various initial bacteria concentrations.

Time after treatment	Initial *E. coli* concentration 10^9 CFU/L			Initial *E. coli* concentration 10^8 CFU/L		
	3 min insertion	5 min insertion	10 min insertion	3 min insertion	5 min insertion	10 min insertion
30 min	100-150	100-150	100-150	90-100	50	45
2 h	100-120	30	3	70	6	5
2 days	15	<1	<1	2	<1	<1
3 –20 days	<1	<1	<1	<1	<1	<1

The results of tests of the experimental device with alloy electrodes that were performed at the Department of Pathology of the University Sains Malaysia are shown in Table 5. "No growth" was reported for each of the samples compared to mixed coliform growth in the control (*i.e.,* untreated) samples.

Table 5. Test results of the portable experimental device conducted at the Department of Pathology of the University Sains Malaysia.

Post-treatment duration	Contaminated water treated with device	Contaminated water	Uncontaminated water
0 h	Mixed coliforms	Mixed coliforms	Mixed coliforms
1 h	No growth	Mixed coliforms	Mixed coliforms
3 h	No growth	Mixed coliforms	Mixed coliforms
1 day	No growth	Mixed coliforms	Mixed coliforms
1 week	No growth	Mixed coliforms	Mixed coliforms

In the Aral Sea region, disinfection devices using solar-energy batteries were installed and tested on manual water pumps. In these devices, the instantaneous value of electric current I between the electrodes was regulated automatically by using a water flow meter to satisfy the following formula:

$$I = \frac{C}{E}\frac{\Delta V}{\Delta t} \approx 0.043\frac{\Delta V}{\Delta t} \quad (3),$$

where **C** is the most effective concentration of metal ions in water, which, in this case, corresponds to 30 μg/L Ag^+, E=0.7 mg/C is the empirically found value of the electrochemical equivalent of Ag^+ for the water in the Aral basin region, $\Delta V/\Delta t$ is the instantaneous value of flow rate in L/s. In this device, the maximum value of electric current corresponding to the instantaneous peak value of water flow rate 1 L/s was 50 mA and the average energy consumption did not exceed 0.5 Wh.

Year-long field tests of the water disinfection devices described were conducted by the Central Sanitary and Epidemiological Laboratory of the Ministry of Defence of Uzbekistan. In summer time, the initial concentration of bacteria in drinking water in Uzbekistan can increase up to 28 CFU/L. Field test results of the device with a solar battery that was used for additional disinfection of drinking water are shown in Table 6. As can be seen, there were no bacteria in the treated water. The most effective concentrations of silver, copper and gold in treated water were 30 μg/L, 7.5 μg/L and 0.075 μg/L, respectively, which are all less than current drinking water regulation limits.

Table 6. Test results of the device with a solar battery.

Initial concentration *E. coli*, CFU/L	Post-treatment time		
	15 min	1 h	2 h
28	2	0	0
15	1	0	0
11	1	0	0

CONCLUSIONS

The test results obtained demonstrate the efficacy of the water disinfection method based on electrochemical release of Ag^+, Cu^{2+}, and colloidal Au.

The devices utilizing solar batteries as an energy source can be used for preventing bacterial contamination in potable water systems, water storage systems, etc., especially in remote regions with a hot climate.

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PART III

TOOLS AND METHODS FOR ACHIEVEMENT OF HIGH TECHNOLOGICAL PARAMETERS OF WATER PURIFICATION AND WASTEWATER TREATMENT

WATER SAVINGS AND REUSE IN THE TEXTILE INDUSTRY

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ABSTRACT

Water savings, reclamation and reuse in industry are topics of increasing economic interest due to increasing water scarcity and costs. For this reason, research and development activities within this topic is increasing, methods and tools for analyzing water savings and reuse possibilities are being developed, and solutions are being implemented.

This paper presents experience and results of water savings and reuse in industry exemplified by the textile industry. Textile processing is one of the largest and oldest industries worldwide and responsible for substantial resource consumption and pollution. The wet processing part of the industry, i.e. pre-treatment, dyeing, printing and finishing, is especially polluting and resource consuming in terms of water, energy and chemicals. It entails a vast variety of water consuming processes, and like in most industries, freshwater is used in all processes with almost no exceptions.

It was known for many years that fresh water is not needed by all processes taking place in textile wet treatment. However conservatism and consideration for product quality in the industry have until recently prevented substantial water reuse from breaking through in practice. A four year research program on industrial water reuse, however, recently resulted in a break-through of water reuse in the Danish textile industry: one polyester dye-house has since 2001 successfully implemented direct water recycling, saving more than 40 % of water required. Process Integration and water pinch techniques were used to identify the potentials and, combined with the company's process insight, used to achieve the best system design for the reuse of water, energy and chemicals. Separation techniques like membrane filtration have been applied successfully to the process water used in wet

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processing in both cotton and polyester dyeing. Pilot scale demonstration plants have documented the technical feasibility of water reclamation by this technique, with payback periods of 1-3 years. This payback has, however, so far prevented full-scale implementation.

INTRODUCTION

This paper presents an approach to water savings and reuse in the wet treatment part of the textile industry and newly tested options for water savings and reuse. It is based on an insight into wet treatment processes in the industry gained through 15 years of work for and with the textile industry in many countries. The approach, generalisations and option identifications are, thus, based on knowledge of textile wet treatment and water management in over 60 companies in 10 countries mainly in Europe and the Southern African region. Through this work, including many years of collaboration with experts on wet treatment processes at knowledge centres in various countries, a general understanding of technological opportunities and their feasibility has been developed.

Our experience base is research and technology development, -transfer and - implementation within the following contexts and relations in particular:

(i) the Danish Cleaner Technology program for the textile industry funded by the Danish Environmental Protection Agency, and co-operation with a large number of Danish textile companies within this program;

(ii) the Danish program for technology transfer to Eastern Europe funded by the Danish Environmental Protection Agency, and close co-operation with the textile research institute in Lodz, Poland and a large number of Polish textile companies;

(iii) close co-operation with the Danish Technological Institute, especially the head of the textile department, John Hansen, for 15 years;

(iv) close co-operation with the Pollution Research Group (PRG) of KwaZulu Natal University in Durban, South Africa, especially the head of PRG, Professor Chris Buckley, for 10 years;

(v) the Danish Centre for Industrial Water Management, and within this centre 4 years of close co-operation with the polyester dye-house of Trevira Neckelmann A/S, especially the Environmental Manager, Palle Nelleborg and Project Manager Kresten Karlsen;

(vi) the European 3 year research project INNOWASH;

(vii) the Cleaner Textile Production Project in the South African Textile Industry, funded by the Danish foreign aid organisation DANIDA.

Some of the most recent and in-depth research has been done within the Danish Centre for Industrial Water Management (Danish acronym CEVI, website www.cevi.dk). The centre homepage can be visited for information on the research results, centre partners, etc. Through this research centre, further options for water savings and reuse in industry were developed, including new options in textile dyeing.

Water costs are steadily increasing. One reason is increasing water scarcity in some regions and urban areas, another is increasing treatment costs in municipal systems downstream. Moreover, water has developed into an object of taxation for both local and national authorities. Table 1 illustrates water costs within a number of European countries and Table 2 shows the development of water costs over time in Denmark.

The development in water costs in Denmark shows an increase in total costs of water intake and outlet of 7-8% per year – occurring during a corresponding inflation rate of 2% and GNP growth rate of 2.5%. In other parts of the world, the increase has been even larger than this, e.g. in South Africa, where a current total water cost increase of 11-12% per year is experienced at a growth rate in the manufacturing sector of only 1% per year (Schneider 2003). There is, thus, a very significant relative increase in water costs, and the trend is global. This bears huge implications for the water consuming industry, and water efficiency has become a significant competition parameter.

Table 1. Costs of water and wastewater in European countries and USA (Sintra 1999).

Country	Cost of water supply (EUR/m^3)	Wastewater discharge fee (EUR/m^3)	Total cost (EUR/m^3)
Austria	n.a.	n.a	0.69
Belgium (Brussels)	1.48	0.35	1.83
Belgium (Flanders)	1.80	0.63	2.43
Czech Republic	0.32	0.25	0.57
Denmark	0.56	2.00	2.56
England and Wales	1.21	1.42	2.63
Finland	1.05	1.28	2.33
France	1.34	1.29	2.63
Germany	1.43	2.19	3.62
Greece	0.69	0.27	0.96
Hungary	0.40	0.29	0.69
Italy	0.43	0.28	0.71
Luxembourg	n.a.	n.a.	0.85
Switzerland	1.09	-	1.09
Scotland	0.71	0.50	1.22
Spain	0.60	0.30	0.90
Sweden	n.a.	n.a.	2.46
The Netherlands	1.19	1.48	2.67
USA	0.49	0.57	1.06

Water costs in the company derive from several cost elements related to water intake and water preparation, use and discharge. Total cost and saving potentials related to water management therefore exceed the intake and outlet costs shown in Tables 1 and 2. In Table 3 below, a total of 6 cost elements related to water are identified, and examples of unit costs given.

Table 2. Developments in water costs in Denmark (Svendsen et al. 2000).

Year	Water supplies behind data (No.)	Water supply, EUR/m^3			Wastewater discharge, EUR/m^3		
		Mean	Min.	Max.	Mean	Min.	Max.
1991	116	0.40	0.11	1.01	1.07	0.23	2.44
1992	12	0.40	0.11	1.06	1.13	0.34	2.58
1993	120	0.42	0.13	0.85	1.27	0.40	2.97
1994	134	0.43	0.07	1.01	1.29	0.40	2.97
1995	142	0.44	0.07	1.11	1.39	0.43	2.97
1996	158	0.48	0.07	1.52	1.43	0.41	3.10
1997	172	0.47	0.07	1.40	1.58	0.64	3.26
1998	125	0.50	0.16	1.62	1.73	0.98	3.38
1999	101	0.52	0.14	1.45	1.85	0.87	4.39
2000	101	0.56	0.14	1.55	2.00	0.99	4.39

Table 3. Cost elements and unit costs for industrial water consumption and discharge: typical costs of individual water streams in the Danish textile industry.

Cost element	Cost (€/m^3)
1. Water intake	0.2 – 0.5
2. Water preparation (e.g. softening)	0.0 – 0.5
3. Energy content	0.0 – 2.0
4. Chemical content	0.0 – 5.0
5. Water discharge	1.5 – 4.0
6. Contaminant specific fees (COD, SS, N, P)	0.0 – 15.0
In total	1.7 – 27.0

The water related costs could be broken down to each individual process/water stream in the company. The basic costs are water intake and discharge being fixed costs per m^3. Depending on the process/stream, additional costs may come on top of these like costs for softening, if the process requires soft water, and energy, if the process requires hot water. In case a hot, soft water stream can be reused, saving potentials are equal to water intake, softening, heating and discharge. Some streams may contain residual chemicals of a certain value, if the stream and its chemical content can be utilised. Examples are water streams with residual pH buffering chemicals, oxidising agents or surfactants. If an alkaline or acid stream is recycled, this may, moreover, lead to savings in end-of-line neutralisation of total wastewater. Finally, many companies pay extra fees for specific wastewater contaminants like COD, suspended solids (SS) and nutrients (N and P). Such contaminants can have very high concentrations in individual water streams and the cost contribution from these streams equally high. Therefore, the variation in costs and saving potentials on reuse is as high as illustrated in Table 3 between individual streams in the company. The implication of this is that seeking cost-efficient options for water savings and reuse is a stream-by-stream issue.

STRATEGY FOR WATER SAVINGS AND REUSE IN TEXTILE WET PROCESSING

Measures for resource savings and environmental improvements in the company are always a part of holistic production optimisation efforts and always subject to cost/benefit considerations. Any measure should be feasible and economically attractive with sufficiently short payback from its own costs and benefits or it should constitute the best way of meeting a precondition to produce (e.g. meeting requirements of discharge permits). Another driver would be a competitive advantage and increased market share influencing the overall cost/benefit ratio of the company (e.g. by meeting customer requirements or achieving eco-labels).

Water management and water savings in a textile company are, therefore, subject to cost/benefit considerations, and a holistic and prioritised approach should be taken to ensure the best cost/benefit ratio in achieving water efficiency in wet processing. The elements of such an approach are shown in Table 4. The elements are listed in order of priority.

First, the experience is that the best cost/benefit most often lies in possibilities for savings of water and waterborne energy and chemicals by process alterations within the existing equipment. Measures at this level do not imply large investments and should often be carried out before any new investments, including new production equipment or equipment for water collection for recycling or treatment, are considered. There is no reason to invest in equipment for water volumes that could be avoided by simple savings.

Second, rebuilding or renewing equipment to achieve higher water efficiency and higher productivity often pays off better than investment in equipment for water handling alone. Therefore, such modernisations of equipment should be considered prior to any equipment for water management.

A measure more independent of water management priorities is the substitution of chemicals with more environmentally benign ones. This is an ongoing process driven by environmental legislation, technical developments in the chemical industry and customer preferences. There is, however, a link

Table 4. Elements of the environmental engineering & water management in water consuming industry.

The 7 Re's	Content of the element	Environmental Engineering Tool
1. Reduce	*Optimisation:* Possibilities for savings in water, energy and chemicals within existing equipment	Process intensification
2. Rebuild & renew	*Modernisation:* Possibilities for improvements by rebuilding or renewing old equipment	Process intensification
3. Replace	*Chemical substitution*: Substitution of hazardous chemicals by less hazardous chemicals	Chemical substitution
4. Reuse	*Direct water reuse:* Collection and reuse of water and waterborne energy and chemicals	Process integration
5. Reclaim & reuse	*Water reclamation and reuse*: Collection and upgrading of water prior to reuse of water and waterborne energy and chemicals	Process integration
6. Recover	*Energy recovery:* Recover energy in water streams by heat exchange	Process integration
7. Remove	*Water treatment and discharge:* Collection and treatment of water prior to discharge	Effluent treatment

to water management, because the presence of certain chemicals in the water can be both barriers and incentives for water reuse. Therefore, as a third element, chemical substitutions should always be considered prior to or in parallel with water reuse measures. There is no reason to battle with chemicals that are detrimental to water reclamation and reuse, if such chemicals could be avoided by beneficial substitution.

Fourth, water reuse can be considered. Having explored options within the first three mentioned elements, the remaining water consumption and effluent factor is likely to be the volume necessary to run cost-efficient wet processing in each individual process. Further water efficiency may, however, be achieved by cross-utilisation of effluent streams between processes. In textile wet processing companies, it is often realistic to reuse around 30% of the water directly with no prior treatment for upgrading, just by collection and making use of individual water streams in processes that do not need fresh water quality. Of course, this most often involves a better cost/benefit than having to upgrade the water-by-water reclamation technologies before reuse, and such possibilities should, therefore, be explored before any investments in water reclamation are considered.

Fifth, water reclamation for reuse can be considered for water streams that cannot be reused directly as they are.

Both direct water reuse and water reclamation and reuse imply potential savings on water as well as waterborne energy and chemicals. In case the energy content of the stream in question can be made use of by the receiving process, the efficiency of energy recovery is 100%, and on top of this is the value of saved water and effluent discharge plus any chemical savings. Therefore, water reuse either directly or subsequent to reclamation involves much higher saving potentials for the same stream than energy recovery by heat exchange. This is why energy recovery is listed as the sixth priority only, being mainly relevant for streams with no possibilities for water reuse.

The seventh priority is water treatment for discharge implying only costs and no economic benefits other than those related to overall environmental performance and compliance.

The approach for water savings and reuse in the textile industry illustrated here implies working upstream, where water characteristics are still process specific, and not downstream, where sub-streams have been mixed and water characteristics represent an overall average.

The final choice between options for savings on water and waterborne energy and chemicals is, of course, subject to an overall technical and economic feasibility assessment. It will depend on the level of technology at the company in question how many options are left to find at the various levels of intervention in the prioritised list.

WATER SAVINGS BY PROCESS INTENSIFICATION

Process Intensification is essentially a matter of maximising resource efficiency and minimising waste generation per functional output from the process. This is an everlasting aim of companies and suppliers of process technology and equipment.

In textile wet treatment, a core issue has been the so-called liquor ratio of the machinery, being the water consumption per kg of fabric in each operation. Minimising the liquor ratio has been a major guiding star in machinery development and, as an example, batch dyeing machines for knitwear (see Fig. 1) have over the last four decades gone from liquor ratios of 30:1 to 6:1 or even lower, i.e. the machine of today does the same job in dyeing or other operations using 6 L/kg fabric as the 30 or 40 years old machine using 30 L/kg. Likewise, research and development of dyestuffs and auxiliaries for textile wet processing have a continuous aim of increasing dyestuff up-take and dyeing efficiency in general.

There is, however, to some extent an in-built conflict of interest in being a chemical supplier and aiming at chemical savings. In the textile industry, the conflict is further exacerbated by the fact that process development and the wet processing know-how to a wide extent lie with the chemical developers and suppliers, because these also develop the dyeing/wet processing recipes within which the chemicals are used. In many cases,

Figure 1. Batch dyeing machines for knitwear.

recipes used in practice today comprise excessive use of chemicals, water and energy.

Example: Recipes in batch dyeing of cotton. In cotton dyeing, a number of rinsing operations are carried out after the dyeing of the cotton in order to rinse out surplus dyestuff that has not established a chemical bond to the cotton fibre during dyeing. In many cases, but not all, the recipe will include one or more “soaping” steps where detergents and complexing agents are added. Experience shows, however, that detergents and complexing agents in rinsing can be left out completely provided a good pretreatment of the cotton is done before dyeing, and provided soft water is used for rinsing (Knudsen and Wenzel 1996) as also shown earlier in lab-scale experiments (Fiebig and Soltau 1989).

Table 5 shows a recipe including several soaping steps and an optimised one without any soapings doing the same job with less than 50% water consumption. Many variants of such possibilities to minimise water, energy and chemical consumption in wet treatment recipes are found in most of the industry.

From the large number of cotton dye-houses visited worldwide, the impression is that around 50% of the companies rinse completely without chemicals using just hot, soft water while the remaining 50% use various amounts of chemical auxiliaries. Rinsing water characteristics will change when leaving out chemical auxiliaries, and changes may, therefore, influence the colour and shade of the fabric. Omitting auxiliaries may, thus, mean adjusting recipes somewhat and is not done overnight. But the cost/benefit of such changes will often be much higher than any water reuse measures.

Example: Counter flow on continuous lines. Continuous dyeing and washing machines (Fig. 2) provide the most efficient textile wet processing due to the counter current principle by which the textile and the water flow through the many compartments of the machine in a counter current

Table 5. Example of process intensification by recipe optimisation in batch dyeing of cotton knitwear.

Batch No.	Existing recipe	Optimised recipe
1	Pre-treatment	Pre-treatment
2	Rinse	Rinse
3	Neutralization	Neutralization
4	Rinse	Rinse
5	Dye-bath	Dye-bath
6	Rinse, cold overflow	Rinse, cold
7	Rinse, 50 °C	Rinse, 95 °C
8	Neutralization, 50 °C	Rinse, 95 °C
9	Rinse, cold overflow	Rinse, 95 °C
10	Soaping, 95 °C	Softening/Neutralization
11	Rinse, 60°C	
12	Rinse, cold overflow	
13	Soaping, 95 °C	
14	Rinse, 60°C	
15	Rinse, cold overflow	
16	Softening/Neutralization	

fashion. Some recipes, however, require very different water characteristics in individual compartments or sections of the machine, while other recipes can accept a water quality gradually changing with the counter flow. The machine can be set to run in full counter flow, semi counter flow, or water in-and-out of each compartment. When time exerts its influence on the daily operation of such machines, there is a tendency that the settings of the machines over time

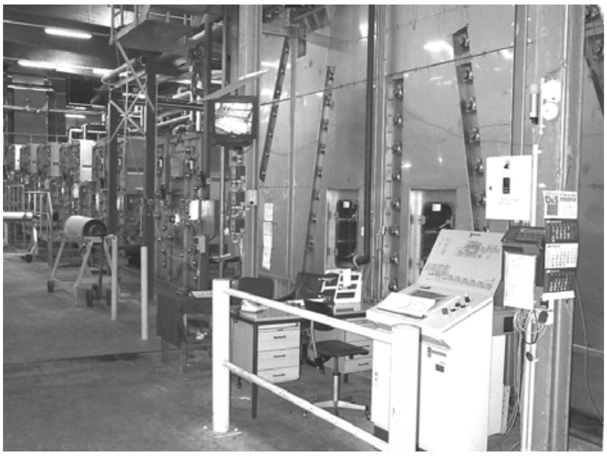


Figure 2. Continuous dye-machine for woven fabric.

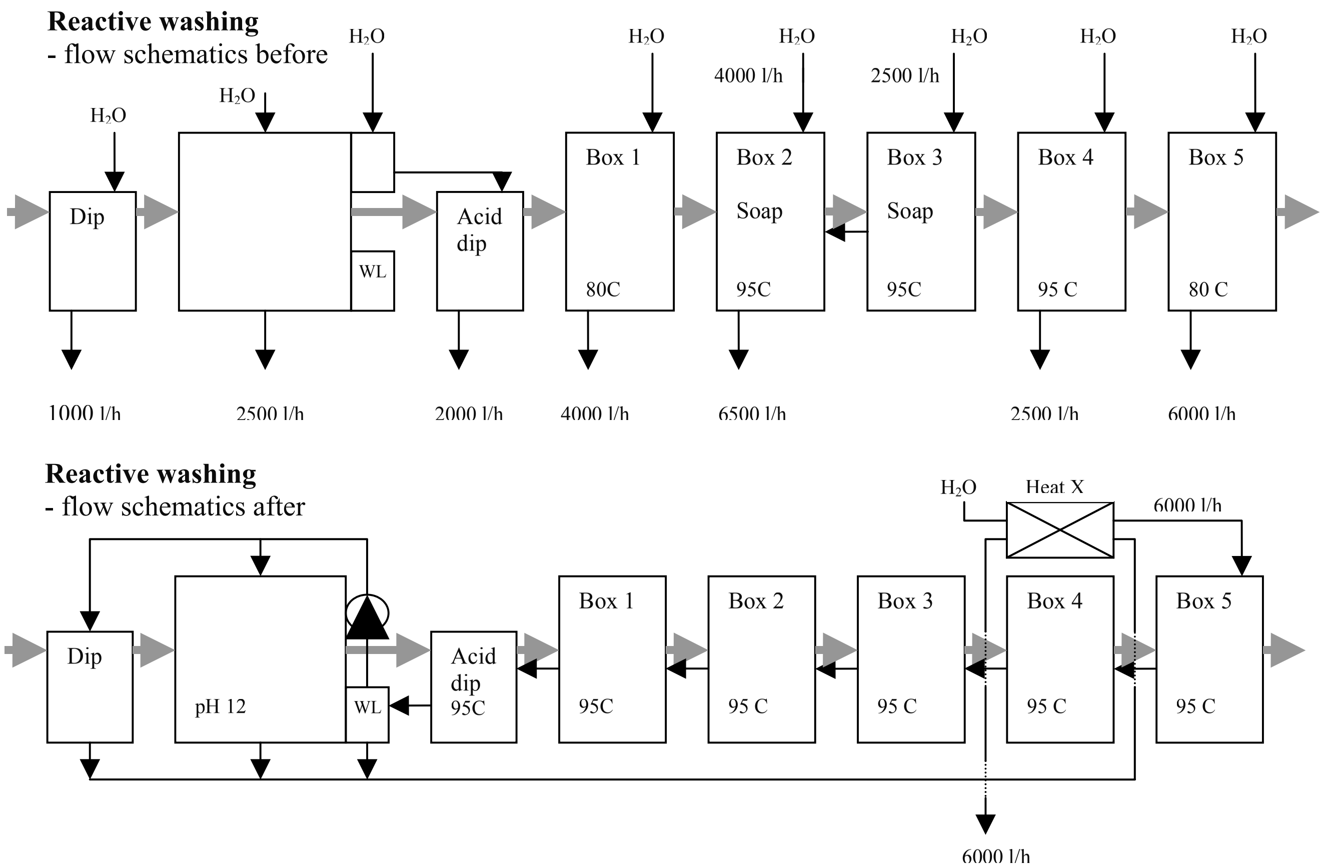
Change to less counter-flow. It is easier to operate a machine with clean water in each compartment, and in the everyday life of the machine operator, there is no reward from resource savings, but a lot of trouble if product quality fails a single time. In most companies, therefore, quite large potentials for process intensification exist in optimising counter flow on continuous machines. Figure 3 shows a real-life example of changing flow schematics to full counter flow in a cotton-washing recipe in a cotton dye-house for woven fabric. Water and energy consumption was reduced by over 60%. Instead of using chemical auxiliaries, hot soft water could be used.

WATER SAVINGS AND REUSE BY PROCESS INTEGRATION

Having explored options for process intensification, further increase of water efficiency by reusing water can be addressed. In most textile wet processing today, fresh water is used in each operation. But many operations do not actually need water of fresh water quality – just imagine the washing process in your laundry machine at home: soon after the washing has started, the water becomes quite dirty, and in reality the washing takes place in dirty water. Water with say 20% of the dirt from the washing goods could easily be accepted without negative impact on the wash result. In textile wet processing, many washing and rinsing operations take place, and many other operations could also accept water of lower quality than fresh water. So a large potential saving lies within using the cleanest of the process effluent streams in processes that can accept these water qualities. Figure 4 illustrates the point. The photos show samples of water effluent streams from a cotton/polyester batch dyeing and rinsing recipe.

It is clear that a lot of quite clean water streams are discharged to the sewer from this recipe, and as it turned out by a closer analysis, a lot of potential "customers" existed in terms of processes that could actually accept the quality of these streams instead of fresh water quality.

The exercise of analysing possibilities for using some process water effluents as other process water intakes belongs to the discipline of Process Integration. In the theory of Process Integration, process water effluents are all available for reuse, and they are named *sources* (of water). Likewise, all operations can in theory accept these sources, and these potential receivers are named *sinks* (of water). Now, each sink will only accept water of a certain quality, and this quality can be precisely described in terms of the *quality constraints* to be met for water accepted by the sink. Process Integration is, thus, the discipline of matching the flows and qualities of sources with the required flows and qualities of sinks and moreover matching them in a way to achieve minimum water consumption – or in practice rather optimal cost/benefit. The theory of process integration is described in literature and both simple graphical (e.g. Wang and Smith 1994, El-Halwagi 1997, Hallal


Reactive washing
- flow schematics before

Reactive washing
- flow schematics after

Figure 3. Process intensification by rebuilding a continuous line and changing flow schematics to full counter flow in continuous washing after cotton dyeing of woven fabric. WL is a water lock (Wenzel and Schneider 2003).

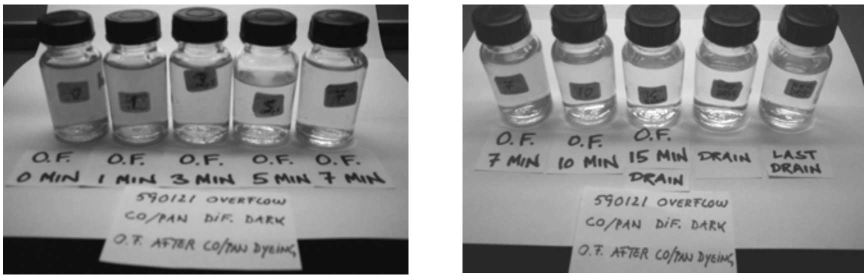


Figure 4. Samples of water effluent streams from a batch cotton/polyester dyeing and rinsing recipe. O.F. 0 MIN, O.F. 1 MIN, etc. indicate that the sample is taken from the overflow rinse after the specified number of minutes. O.F. 7 MIN and O.F. 10 MIN are shown on both photos.

2000, Dunn and Wenzel 2001) and more complex mathematical approaches (e.g. Alva-Argaez' et al. 2000 and Keckler and Allen 1999) exist.

Example: Process Integration in polyester yarn dyeing. An in-depth Process Integration study was performed at the Danish polyester yarn dyehouse Trevira Neckelmann A/S (Wenzel et al. 2001). First an inventory of the water consumption of the company was done revealing the main categories of water consumption (see Fig. 5).

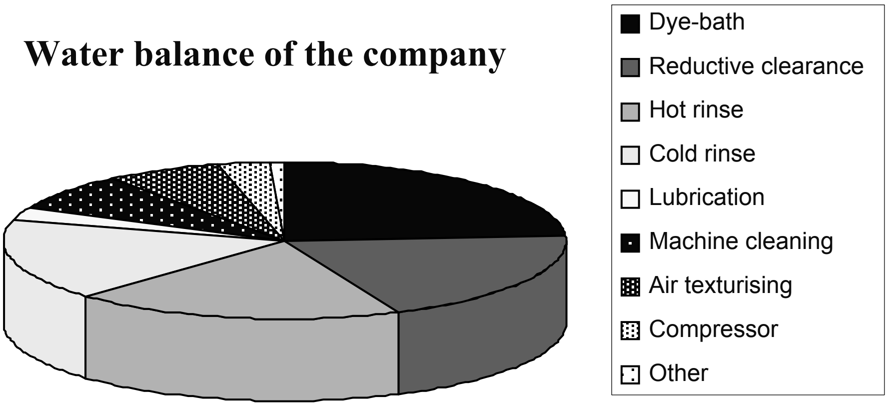


Figure 5. Relative water consumption of the company divided into the main categories.

The majority of water consumption lies within the wet processing in the dyehouse, only water for Air texturising, the Compressor and "other" lie in other compartments of the company. The yarn dyeing in the company is conceptually a very uniform operation using the same overall recipe. The water categories from "Dye-bath" to "Cold rinse" all derive from dyeing by this generic recipe. The "lubrication" is water from a wet yarn oil application process used for some dye-lots only. "Machine cleaning" is water used when the machines are frequently cleaned due to increasing colour contamination of their inner surfaces.

Fig. 6 shows the generic dyeing recipe as it was before any Process Integration was done. Fresh, softened water was used in all batches of the recipe, and all effluents were discharged to the sewer – as conventional for all similar dyehouses. Fig. 6 shows the generic recipe used in all dyeings, but it is a much too simplified picture of the variation of water effluent streams deriving from the dyeing – or *sources* to stay in Process Integration terminology. The library of colours and shades to be met by the dyeing operations contains several thousand individual recipes, and the variability in source flows and qualities is huge, and so – it turned out – is the variability in what water qualities sinks can accept, i.e. the *sink constraints.* A huge number of sources were tested to determine their quality, and likewise the dye-house tested a large number of water types in small-scale test dyeings in order to establish the background for setting sink constraints. Based on this, a so-called pinch analysis was then done, revealing that a theoretical potential of around 50% water saving by reuse existed.

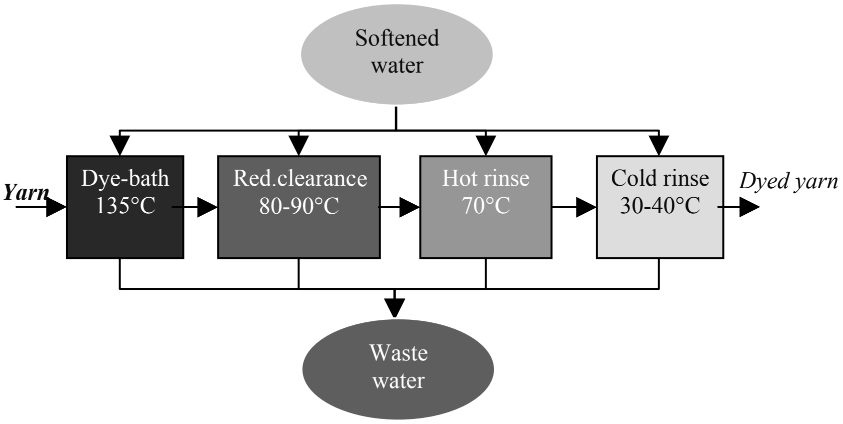


Figure 6. The existing generic recipe for the yarn dyeing before Process Integration.

Several designs were considered to achieve an operable water reuse system getting close to this target with the best possible cost/benefit. Finally, the choice stood between a central design with two larger buffer tanks for reusable water in two qualities, or a de-central solution with two tanks next to each machine, amounting to 26 smaller tanks in total. For reasons of both operability, quality safety, and economy the choice fell on the de-central solution, which was then established, see the photo of one dye-machine and two connected buffer tanks in Fig. 7.

The resulting system design for water reuse can be illustrated by the change in flows within the generic recipe. Fig. 8 shows the essence of the design. It looks very simple, and it is. However there is a bit more to it than shown in the Figure: it is important how the dye-lots are run between machine cleaning operations, and how water is reused in these machine cleanings as well. But the water reuse system has not in this or any other respect implied more constraints to dyeing and cleaning operations than before. An overall water saving of 45% was achieved by this system design and significant energy savings as well, being thus very close to the theoretical target of around 50%. It has been operating since 2001 without problems and with very large economic gains and a payback period of less than a year. The design is believed to be applicable to polyester dyeing in general, and the dissemination potential is, thus, large.

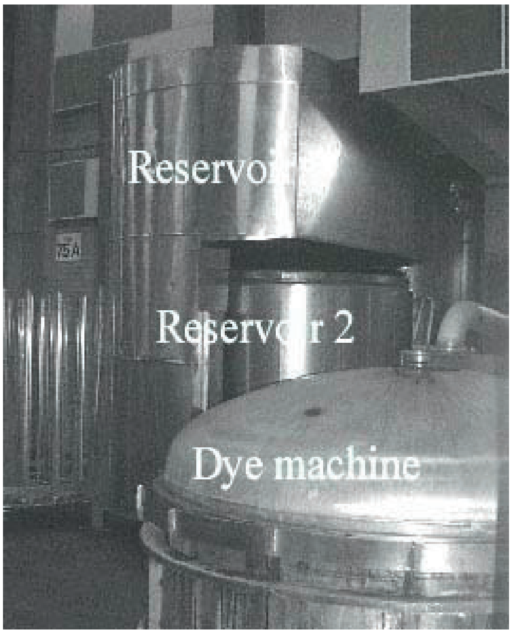


Figure 7. The established de-central water reuse system.

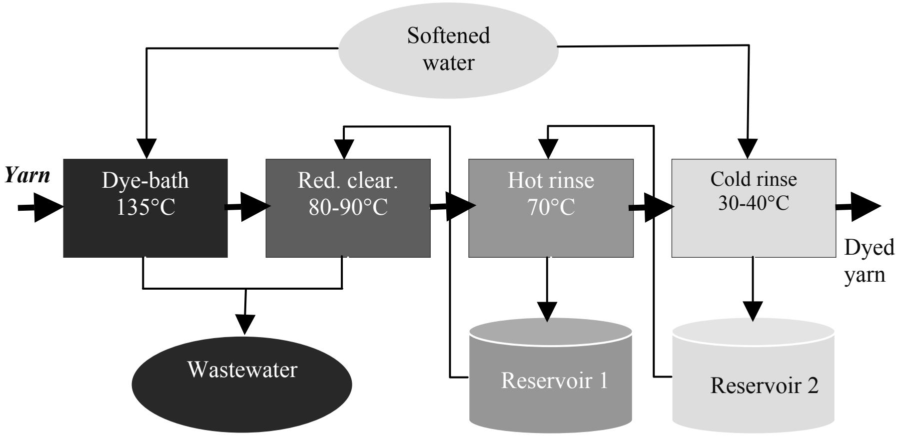


Figure 8. The resulting system design for water reuse in the polyester yarn dye-house.

WATER RECLAMATION AND REUSE

Having explored options for direct water reuse, further increase of water efficiency by upgrading water quality using water reclamation technologies can be addressed. The majority of the water flow in textile wet processing is coloured, and most operations require colourless water. One important requirement to meet the quality constraint of the majority of sinks is, therefore, colour removal.

Several techniques can be considered to remove colour: filtration, adsorption, precipitation and evaporation being some of the most important candidates and the most widely tested.

Example: water reclamation in cotton dyeing. Within a large Danish research program focusing on water reclamation in batch dyeing of cotton, four different techniques for reclamation of water, energy and chemicals were tried out: Chemical precipitation followed by separation, membrane filtration, activated carbon adsorption and counter current evaporation/condensation. A large number of precipitants, membranes and activated carbon products were tested in laboratory scale. The results showed that feasible solutions could be found within the use of either technique. Consequently, the most suitable precipitants, membranes and activated carbon products were picked out for further pilot scale testing. All four techniques were tested extensively including reclamation by evaporation/condensation. These series of tests formed the basis on which to choose the best-suited concept, and furthermore it provided the information needed to design a full-scale plant (Wenzel et al. 1996).

The low salinity rinse water can be treated with all four techniques. However, membrane filtration proved to be economically and technically advantageous compared to the other techniques. Through testing, membranes especially suitable for separating dyestuff from water under the given conditions were identified: Desal DK nanofiltration (NF) membrane and Desal SG reverse osmosis (RO) membrane. It has been demonstrated to be possible and even favourable to operate the filtration at high water temperatures (approx. 90°C), which allows for direct hot water reclamation and reuse. Both the NF and RO membranes produce colourless hot water, the RO membrane desalted water as well, and this technique therefore makes it possible to reuse water and energy (Knudsen et al. 1999). A membrane plant was built at the Danish cotton dye-house Martensens Fabrik A/S for demonstration in a small scale, but in full operation, treating the rinsing effluent from 5 smaller dyeing machines and reusing the permeate for rinsing. The plant was operated for a year, successfully demonstrating the technical and economic feasibility of membrane filtration. A photo of the plant is shown in Fig. 9.

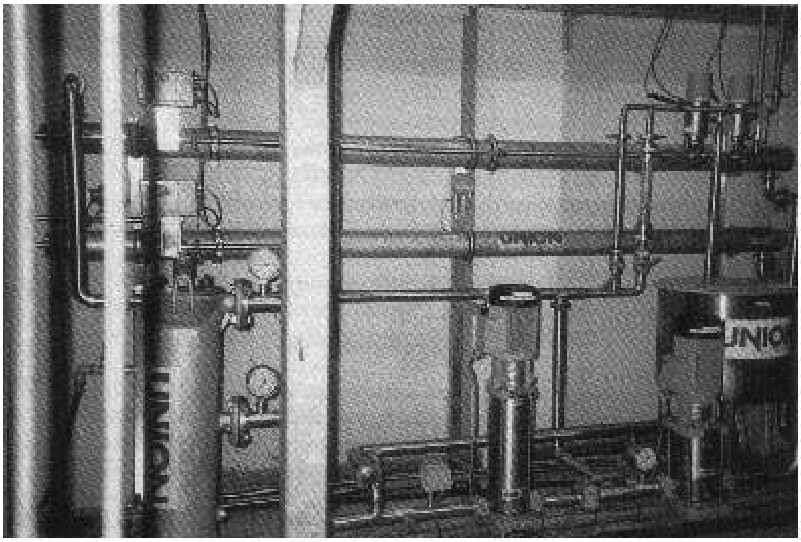


Figure 9. Demonstration membrane plant at Martensens Fabrik A/S.

The plant operated at a high water temperature (around 90^{o}C) and none of the membrane elements were damaged by the hot water. One element, which had been in continuous operation at 80-90°C for at least 4 months – with membrane cleaning once a week - was cut open in cooperation with the manufacturer and classified as undamaged. By running the plant at this high temperature and reusing the hot permeate for rinsing water, it was possible to reuse energy for rinsing fully with no need for heat exchange. This direct application of hot rinsing water was, moreover, demonstrated to save 50% of the time for rinsing compared to the existing recipe in which some baths were cold and others heated in the machine, thus requiring time for heating.

Membrane filtration produces a concentrate containing a high concentration of dyestuff. The volume of this concentrate is around 1-3 % of the original volume of process water, and the concentrate must be disposed of. Lab scale tests have shown that the concentrate can be treated in anaerobic digesters (Wenzel et al. 1996). There is a complete colour removal with no negative impact on the digester when concentrate is fed at up to 20% of the total digester intake. Anaerobic treatment of the concentrate is an environmental improvement compared to the present situation, where the effluent containing dyestuff is typically discharged to conventional aerobic wastewater treatment plants, giving only 50% colour removal.

To document an alternative way of concentrate handling, the concentrate has successfully been treated by activated carbon adsorption. The activated carbon used is of the type F400 from Chemviron, the residence time around 2 hours and the capacity expected around 4 kg carbon/kg dyestuff. The saturated carbon can enter into a well functioning reuse system for regeneration, managed by the manufacturer of the activated carbon.

Operation costs for the membrane plant will amount to approx. 0.75 EUR/m^3 rinsing water, and the maximum investment will be 0.75 EUR/m^3 including pipes, plumbing etc. when amortised over a period of 5 years. This implies a total of 1.5 EUR/m^3 over the 5-year period. These expenses should be compared to the savings in water and energy, which as an average in Danish textile industry is around 3 EUR/m^3. The reductions in production time in the rinsing processes, when using hot water, are 50% (~30% of the total production time for the recipe). The reduced costs due to this reduced production time are estimated to be around 1 EUR/m^3. A calculation of the simple payback period for the membrane plant, as investment divided by savings minus operation costs, shows a payback of less than a year.

Example: water reclamation in polyester dyeing. As an option for “closing the loop” fully in polyester dyeing at the Danish dye-house Trevira Neckelmann A/S, membrane filtration was tested to upgrade the part of the water flow that could not be used directly. The flow schematics were laid out as shown in Fig. 10. Through laboratory and small pilot scale studies (Gottrup and Kringelum 2000) and large pilot scale test by Knudsen et al. (2002), a feasible technical solution to membrane filtration of the most contaminated water streams in polyester yarn dyeing was found. During the research, water contaminants were identified that could act quite detrimentally to the tested membrane modules due to fine particles precipitating in the modules. Various pre-filtration techniques were tested to take out these contaminants before the membrane modules in terms of filter bags and continuous paper filter bands of different pore size, but none of them could remove the particles sufficiently well. Finally, a so-called cross-rotational ultrafiltration concept was tested, which showed very positive results and an ability to keep up the capacity of the UF membranes and preventing particles to pass and enter into the subsequent RO spiral wound membranes. This pre-filtration was documented as technically feasible, and thus a solution concept for closing the loop was found.

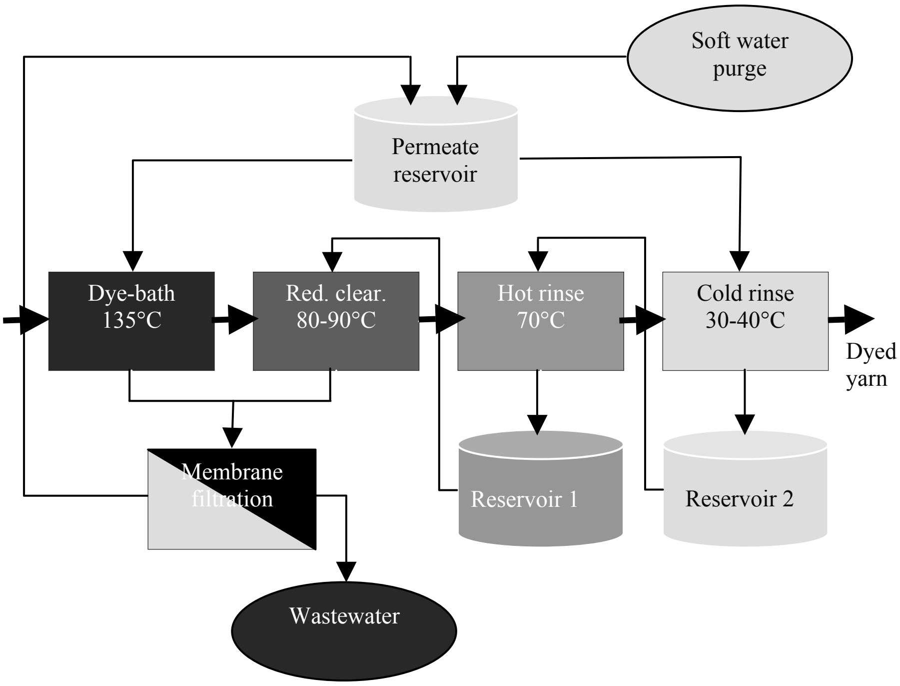


Figure 10. Flow schematics for fully closed loop process integration including direct water reuse and water reclamation by membrane filtration at the Trevira Neckelmann A/S polyester yarn dye-house.

The full membrane plant was found to have a simple payback of 3-4 years, which was too long for the company to invest in the solution at present. The proposed solution, therefore, awaits implementation until a change in economic framework conditions provides somewhat stronger incentives.

CONCLUSIONS

Water efficiency of textile wet processing has gradually increased over the last decades and is still increasing. The main agent has been the improvement of the liquor ratio of dyeing machines. For example, in batch machines for knitwear dyeing, the liquor ratio has gone from 30:1 up to 6:1 or even better for the most efficient machines of today.

Large potentials for increasing water efficiency by process intensification still remain, however, both by optimising batch recipes and by optimising counter flow in recipes on continuous machines. Water saving potentials of 50% can still be found in many recipes in companies around the world.

A saving potential that has not yet been addressed to any substantial degree is saving by process integration, i.e. direct reuse of water streams in wet treatment operations that do not necessarily require water of fresh water quality. Recently, a break-through was achieved in the Danish textile industry, where one polyester yarn dye-house has achieved around 45% water saving by implementing direct water reuse in the dye-house. The solution has been in operation since 2001 with large economic gain, short payback of less than a year and no operational problems. The potential of water savings by developing and implementing such recipe specific water reuse solutions worldwide is believed to be huge and in reality largely unexplored.

Further water savings and “closing of the loop”, by means of water quality upgrading by membrane filtration, has been successfully documented in large pilot scale/small full scale within both cotton dyeing and polyester dyeing. Plants have been documented as technically feasible and the economies have been revealed. The identified payback of 1 year in cotton dyeing and 3 years in polyester dyeing has until now been to high to allow the companies to invest. When economic framework condition due to increasing water costs allows it, these solutions are ready to be implemented.

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BIOCIDE POLYMERS - NEW OPPORTUNITIES IN WATER TREATMENT

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According to the data of the World Health Organization (WHO) experts, the sickness and death rates of the world population could be reduced by 75 % by maintaining the necessary sanitary conditions and the quality of drinking water (Momukalo 2003). The profound studies of causes of diseases, initiated by drinking water, carried out during the last decade support that notion. For example in 1991-2000, in the USA, bacteria caused about 18 % of such illnesses, whereas viruses accounted for 6 %, pathogenic protozoa for up to 21 %, and chemical components for 16 %. Almost 39 % of diseases with typical "water-caused" signs were classified as those "with obscure aetiology" (Strykalenko 2003). That is, drinking water today is considered not only as an essential product for life-support but also as a factor threatening the public health and even life.

According to the public health authorities data, in Ukraine in 2001, one in seven of the water samples taken from industrial and drinking water supply systems did not meet the sanitary-hygienic requirements for chemical characteristics, and one in twelve - on microbiological ones. The chemical pollution of drinking water generates chronic poisoning of the population. At the same time, the problem of microbial pollution, which is manifested as outbreaks of such diseases as cholera, typhoid, hepatitis A and other enteroviral infections, is very severe in Ukraine these days. A consideration of the problem of drinking water quality as a component of national safety testifies to the urgency of this problem in Ukraine (A Decree 2003).

In our opinion, among the reasons causing such a situation in the Ukraine, the following ones should be emphasized.

1. *Water pollution of sources of drinking water supply by non- or poorly-purified wastewaters.* According to the data from municipalities, in the last 10-12 years, the share of polluted waters in the common drainage system has grown by 1.8 times (from 16 % in 1990 up to 28 % in 2001). Twenty-five

A. Omelchenko et al (eds.),
Modern Tools and Methods of Water Treatment for Improving Living Standards, 191–196.

percent of the polluted drainage water gets into reservoirs without any purification, which is 1.6 times higher than in 1990. In addition, 75 % of the sources of drinking water supply in Ukraine are superficial ones.

2. *High degree pollution of natural superficial waters in the Ukraine by organic pollutants of natural and anthropogenic origin.* As a result, the total content of anthropogenic and natural pollution by organic compounds in reservoirs of Ukraine ranges from 6-65 mg/L, i.e., 5-10 times more than in the countries of Western Europe.

3. *The two above-mentioned factors promote high microbiological pollution of the superficial sources of water supply in Ukraine.*

4. *The out-of-date technological processes of drinking water purification,* which are not designed for purification of water with a high degree of pollution by contaminants of anthropogenic and natural origin. The use of chlorine for water disinfection during its purification causes the occurrence of by-products of disinfection in drinking water, such as chloroorganic compounds. Most of these compounds have very strong toxic properties. The application of aluminium compounds as coagulants results in the appearance of aluminium ions exceeding the permissible levels in drinking water, notwithstanding the absence of aluminium in the initial water. It is well known that certain amount of aluminium exerts irreparable genetic damage in humans. Taking into account all the above, the quality of drinking water supplied to the population of Ukraine is alarming. This situation stimulates scientific studies on the improvement of water treatment technologies and the search for new reagents for drinking water disinfection, which are an alternative to chlorine. From the medical, hygienic and epidemiological points of view, the most critical stage of water purification is its effective disinfection.

5. *Deterioration of water networks.* In 1990-2002, the length of water networks, which are in critical conditions, has increased more than 6-fold and comprises 30 % of all networks in Ukraine. The frequent failures at water treatment stations promote pollution of the drinking water (Semchuk 2002). In Ukraine, the application of traditional water purification technologies using chlorine and its compounds for water disinfection from pathogenic microorganisms causes, as is mentioned above, the appearance of chloroorganic compounds in drinking water. The extensive analysis of the products of chlorination of natural waters since 1974, when trihalomethanes were identified in drinking water for the first time, has shown that the application of chlorine for water treatment results in the formation of more than 230 chloroorganic compounds. At present, it has been unequivocally established that the chloroorganic compounds formed in drinking water are carcinogenic, mutagenic, teratogenic, and embriotoxic. They can also suppress the nervous system, generate changes in the blood and the kidneys, cause metabolic disorders, allergies, dystrophic phenomenon in cells, and

cardiovascular diseases. It is noteworthy that boiling chlorinated water can only partially reduce the harmful effects of chloroorganic compounds. Besides, the long-term use of chlorine initiates the inversion of microorganism pathogenesis (i.e., the appearance of tolerant bacteria) and also causes the appearance of other pathogenic factors, which are highly dangerous to humans (Chlorine 2003).

The application of ozone for water disinfection cannot be considered as an alternative to chlorination, as the products of ozonation have a level of toxicity similar to chloroorganic compounds. Besides, ozone application complicates the subsequent processes of water purification and results in the formation of biologically unstable water at the water treatment stations. Also, it is well known that water ozonation does not preclude the use of chlorine at the final stages of purification and this again results in the formation of significant amounts of chloroorganic compounds.

Since the superficial water sources in Ukraine are characterized by a high content of organic compounds of natural and anthropogenic origin, the use of oxidizing reagents for disinfection of such water is only partially acceptable as it results in the formation of highly toxic by-products. Accordingly, the search for alternative technologies for drinking water preparation using reagents having non-oxidizing action is urgent and vitally necessary for Ukraine. Therefore, the application of an essentially new technology using the biocide polymer reagent “Aquaton” based on guanidine compounds is worthy of special attention. This reagent was developed by the Scientific-Technological Centre (STC) “Ukrvodbezpeka”. During a number of years, the properties of guanidine biocide polymers were investigated and the manufacture of the “Aquaton” reagent was organized.

The studies carried out at the Institute of Epidemiology and Infectious Diseases and other leading research institutes of Ukraine have shown that “Aquaton” provides reliable water disinfection from viruses and heminthes (intestinal parasites), and its presence post treatment prevents a secondary growth of microorganisms in water and suppresses the biofouling processes occurring in hydraulic engineering structures.

This reagent dissolves well in water, which makes it even more attractive for application in water treatment technology. Solutions of “Aquaton” do not have any smell; they are colourless and non-volatile, reliable and safe during application, transportation, and storage. They are not corrosive with respect to hydraulic equipment. “Aquaton” is environmentally benign since it is biologically decomposed in the environment. Table 1 shows the comparison of reagents for water disinfecting chlorine, ozone and “Aquaton”. It is clear that reagent “Aquaton”, in many cases, is advantageous as compared to traditional reagents for water treatment.

Table 1. Comparison of reagents for water disinfecting.

Properties	Chlorine	Ozone	Aquaton
Disinfecting	+	+	+
By-product absence	-	-	+
Preservation	+/-	-	+
Stability	-	-	+
Absence of corrosion activity	-	-	+
Flocculative properties	-	-	+
Clearing from heavy metals	-	-	+
Safety at transportation, storage, and application	-	-	+

In the laboratories of STC “Ukrvodbezpeka” and the Desnianskaya Water Station, year-round studies of the effect of “Aquaton” on natural waters have been conducted. Reliable disinfection and a high degree of river water purification were demonstrated. It was found that “Aquaton” is an effective cationic flocculant that lowers the turbidity, the concentration of residual aluminium and improves the water colour. “Aquaton” is similar, in terms of flocculation ability, to the best cationic flocculants of leading foreign firms, and surpasses them in some other parameters. The use of “Aquaton” for water treatment significantly reduces the application of coagulants. Having a high complex-forming ability, “Aquaton” effectively removes organic contaminants from water, e.g., humic substances, and cations of heavy metals. The basic parameters of technology utilizing the “Aquaton” reagent were thoroughly tested using standard equipment. It was unequivocally shown that chlorine could be completely replaced by the reagent in the primary chlorination stage.

To test the disinfecting and flocculation properties of the “Aquaton” reagent in conditions, which are as close as possible to those found in industry, a pilot flowing unit with a capacity of 2.2 m^3 of water per day was designed, assembled and put into operation at the Water Station “Desnianskaya” of the State Utilities Company “Kievvodokanal”. The trials included all the basic units of the water purification system of the station and completely simulated real conditions of the water purification process. Continuous operation of the pilot unit for 11 months confirmed the disinfecting reliability and high level of river water purification using the "Aquaton" reagent. The purified water met all drinking water quality standards.

The trials conducted, using the pilot flowing installation, have shown that application of the "Aquaton" reagent for water treatment, along with purification and disinfection, solves a lot of complex problems accompanying water treatment. Namely, it (i) prevents deposits, which are formed during water purification, from rotting, (ii) suppresses biofouling processes (iii) significantly lowers corrosion of the equipment, (iv) improves the working conditions of the personnel, and (v) makes the water treatment technology ecologically safe.

The disinfecting and flocculation actions of the "Aquaton" reagent were tested on various types of waters from different rivers, such as Desna, Dnieper, Southern Bug, and Teterev and on water from artesian wells. Even at high levels of chemical and biological pollution of the superficial waters, a reliable disinfection level and high degree of water purification was achieved. It is noteworthy that the technology of drinking water preparation using the "Aquaton" reagent fits well into the technological schemes of working water stations and does not require significant reconstruction. As a result of toxicological, hygienic, sanitary and chemical analysis and technological tests, the "Aquaton" reagent is recognized to be safe for humans and its use in drinking water preparation is permitted by the Ministry of Public Health of Ukraine. The analytical method for detection of this reagent in drinking water was developed and certified by the State Standard Organization of Ukraine.

Thus, the biocide polymeric "Aquaton" reagent developed in STC "Ukrvodbezpeka" is the perspective reagent with a complex action of non-oxidizing nature and its application for water treatment can ensure high standards of drinking water along with economical functioning of the drinking water supply systems (Marievsky and Bondarenko 2001).

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OPTIMIZATION OF GALVANIC WASTEWATER TREATMENT PROCESSES

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ABSTRACT

The study is focused on the possibilities for the development and practical application of preventive measures for optimization of galvanic wastewater treatment processes in Lithuania. The results of modernization of the wastewater treatment plant in JSC "Vilniaus Vingis" and optimization of the galvanic technological processes and reconstruction of the wastewater treatment plant in JSC "Vingriai" are presented.

ELECTROPLATING ACTIVITY IN LITHUANIA

In the 1980s, the machine building and instrument making industry took a leading role in Lithuania. Its production accounted for 25% of the total manufacturing and for nearly 20% of the labor force engaged in industry. The growth of all branches (e.g., electronics, electrical engineering, machine building, and metal finishing) was the most intensive. About 15% of the Lithuanian companies had electroplating divisions and more than 10^6 m^2 of material were coated by metal plating per year. A significant amount of salts, acids and alkalis were used for this purpose (Šalkauskas and Klimantavičiūtė 1990).

In the early 1990s, the electroplating industry incurred losses. For example, due to the changes taking place in the market, insufficient level of engineering and other reasons, the volume of galvanic production decreased more than 10 times. Recently, the situation started to improve. Currently, there are 22 companies in Lithuania, which operate in the area of metal finishing. The following processes are widely used: chromium, nickel, and zinc plating (including hot zinc plating), oxidation and coating by tin and lead.

A. Omelchenko et al (eds.),
Modern Tools and Methods of Water Treatment for Improving Living Standards, 197–208.

In comparison with other European countries, metal finishing activities in Lithuania have a competitive advantage in terms of labor costs (Seputis 2002). Therefore, Lithuania is able to compete with other European countries in this sphere of activity.

Currently, the non-compliance of metal finishing activity with existing Lithuanian environmental requirements is the major problem. Old and worn-out equipment for galvanic processes, including galvanic wastewater treatment processes, are the main sources of environmental problems, such as inefficient use of raw materials and energy resources, high volume of waste, sludge generation and insufficient level of wastewater treatment. Companies must solve these problems by application of preventive methods (Kliopova 2002).

CLEANER PRODUCTION METHODS FOR ELECTROPLATING PROCESSES

The typical metal finishing process is presented in Fig. 1.

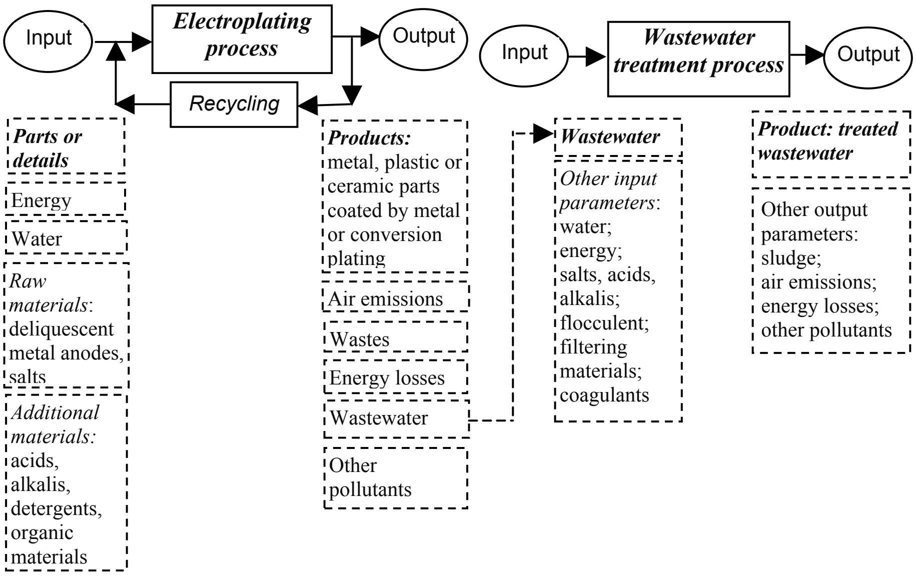

Figure1. Typical metal finishing process.

The waste volume and toxicity depends on many factors. For example, the composition of generated wastes could depend on input materials and the level of technological processes used (Staniškis et al. 2002). The large amount of pollution (wastewater, sludge, energy losses and other) could be generated due to inappropriate choice of technology, obsolete equipment and/or wrong choice of the process control equipment or system (Fig. 2).

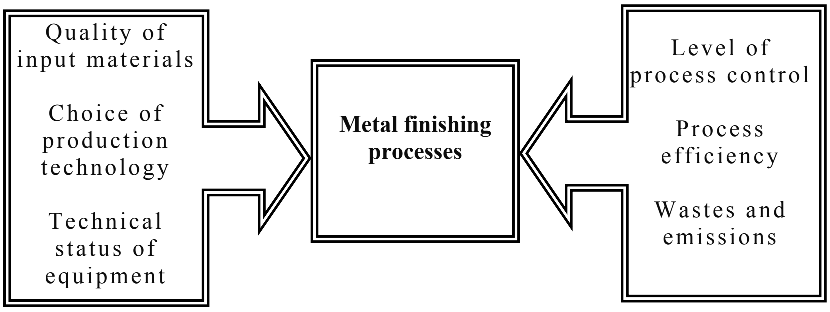

Figure 2. Assessment of the reasons for the possible environmental problems in metal finishing processes.

Due to the above-mentioned reasons it is very important to carefully evaluate the possibilities of different environmental strategies. The general principle of cleaner production (CP)/pollution prevention concept is *to evaluate technological processes for the identification of the problems' source before generation of some environmental ideas to find the best available solution*. The detection of materials which can contaminate the environment and minimization (or full elimination) of these materials constitutes the basis for preventive activity.

The material and energy balances should answer the following important questions: (i) where is the pollution generated? (ii) where do energy losses occur? (iii) what are the causes of the pollution and the energy losses? In addition, the material and energy balances are used for the economic evaluation of technological processes and for estimation of the economic costs of "production of pollutants" (Staniškis et al. 2001).

Fig. 3 presents major pollution prevention measures, which could be applied to all technological processes. CP implementation practice in the Lithuanian Machine and Instrument Industry shows that the environmental problems in galvanic wastewater treatment plants could be solved after, or simultaneously with, evaluation of the electroplating processes. The novel CP engineering techniques implemented helped to optimize some electroplating processes. They clearly demonstrated that using obsolete wastewater treatment processes is not economically or environmentally feasible due to ineffective consumption of energy, raw and other additional materials.

The most usable pollution prevention methods in Lithuanian galvanic companies and examples of their implementation are as follows:

(a) Input substitution. This method requires a number of laboratory analyses to be carried out. As examples, the implementation of electric heating systems instead of steam for bath heating, using less contaminating citrate instead of glycine in nickel-plating processes (Tarozaite and Gylene 2002) and using alkaline solution in zinc-plating processes instead of ammonia solution could be mentioned.

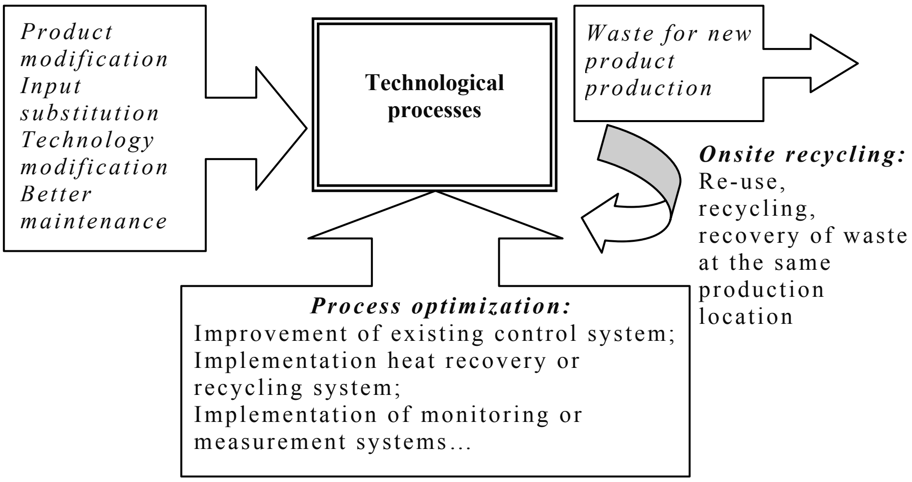

Figure 3. General cleaner production (CP) methods.

(b) Technology modification. This method is associated with large investments for market research, purchase of new technology and implementation. The implementation of electrochemical burnishing processes instead of chemical burnishing or tin/lead plating processes, elimination of hazardous cadmium in plating processes and implementation of powder dyeing technology instead of some electroplating processes exemplify this method. These modifications to electroplating processes make a direct impact on galvanic wastewater treatment. Therefore, technology modification is the most usable CP method in wastewater treatment processes. For example, after the modernization of electroplating processes in JSC “Baltic Vairas” it was decided to eliminate Ni- and Cr-plating and to optimize the phosphotation process (Bagdonas 2003). The optimization of the wastewater treatment plant was the next modernization step: a new coagulant was selected for better precipitation of sediments.

(c) Modernization of worn-out technological equipment. For example, new galvanizing baths with measurement and control systems, and new press filters instead of vacuum filters for sludge dewatering (dehydrating) have been implemented. The last innovation improved the galvanic sludge dewatering process by approximately 15 % (the water volume in sludge was decreased from 70% to 55 - 50 %) (Bagdonas 2003).

(d) Process optimization. This method could be exemplified by the following measures: (i) installation of a conduction sensor or meter allowing control of solution concentration and implementing recycling systems in electroplating processes (Kliopova 2002) (ii) installation of a control reservoir with a pH meter in the filtrate drainage line allowing quality control of the wastewater filtering process and minimization of some accidents (Kliopova 2002); (iii) installation of an automatic chemical dosage system allowing minimization of consumption of raw and additional materials in the wastewater treatment process. Due to optimization of the galvanic wastewater treatment process, the quality of treated water could be suitable for re-use in the galvanic technological processes.

EFFICIENCY OF CLEANER PRODUCTION MEASURES IN LITHUANIAN GALVANIC COMPANIES

The environmental and economic efficiency of the implementation of pollution prevention techniques was analyzed by taking into account the results of CP innovations implemented in the Lithuanian Machine and Instrument Industry during 1998 - 2002. Ten companies from this branch of industry took part in different CP, CP financing and Environmental Management System (EMS) implementation programs that were organized by APINI. Five companies chose the galvanization department as the potential subject for CP evaluation. A summary of the results of environmental evaluation of six implemented CP innovations is presented in Table 1.

Table1. Environmental benefits of CP implementation in Lithuanian galvanic companies (1998-2002).

Environmental sector	**Environmental benefit, units/year**
Electricity saving	890 MWh
Heat energy saving	4,443 MWh
Minimization of chemical consumption	26.7 t
Water saving, wastewater minimisation	26,000 m^3
Minimisation of wastewater pollution:	110.2 kg (P (3.5 kg), Ni (7.5 kg), Cr (9/6 kg), Zn (11.3 kg), Cu (4.5 kg), Fe (70.7 kg), Cd (3.1 kg))
Waste minimisation, including sludge	31.5 t
Minimisation of air emissions in production facilities and wastewater treatment plants	8.6 t
Minimization of environmental fees	30,000 LTL

Total investments in modernization and optimization were about 3,000,000 LTL (868,600 EUR), and total profit - about 1,200,000 LTL (347,500 EUR) (Kliopova 2002).

Innovations costing up to 55,000 EUR are usually implemented using the company's resources. For implementation of bigger projects, the companies began looking for external financing: for example from banks and environmental funds. At present, there are a lot of possibilities to receive subsidies or loans on favorable terms to finance environmental projects, especially for CP projects, which have real economic effect.

Since 1998, APINI has collaborated with NEFCO (Nordic Environment Financial Corporation), which funded a CP investment credit line in the Baltic States. The main objective of these NEFCO activities is to finance implementation of CP projects on favorable terms (Kliopova 1999).

APINI specialists prepare CP investment projects in accordance with NEFCO requirements, carry out monitoring of CP project implementation, and evaluate real environmental and economic benefits after project completion. At present, four CP projects in galvanic and wastewater treatment have been funded through NEFCO's loans.

CASE STUDIES

Modernization of the wastewater treatment plant in the galvanizing department at JSC "Vilniaus Vingis"

Project description

Worn-out wastewater treatment equipment at the metal coating workshop constituted the main problem in the television equipment manufacturing company "Vilniaus Vingis". After the implementation of a rinsing water recycling system in the electroplating processes in 1997, water consumption, wastewater volume and pollution by zinc and nickel decreased. Therefore, it was not economically feasible to use the old wastewater treatment plant due to ineffective use of energy and production facilities.

Modernization of the wastewater treatment plant was completed in September 1999. Comparison of the old and the new implemented technology, and the benefits obtained from implementation are presented in Tables 2 and 3.

Table2. Technical evaluation of modernization of the wastewater treatment plant.

Old technology	New implemented technology
Chromium, acidic and alkaline water was collected into separate tanks.	Wastewater is collected into one tank.
Reagents were supplied into the chromium neutralization reactor by means of a pump. Neutralized water from the reactor was supplied to the intermediate tank and then to another tank in order to settle heavy metals.	Reagents (NaOH, $Fe(OH)_2$, flocculants) are supplied to the reactor by gravitation flow. Solution for neutralization is removed from collection tank in portions. After the full neutralization, wastewater is transferred by gravitation flow to the intermediate tank for sludge separation using a vacuum filter.
Neutralized water was treated by sand filters.	One polyester filter is used instead of 8 sand filters.
Sludge was separated from liquid by old pressure filters. Dried sludge was placed in containers.	One vacuum drum filter BOR is used instead of a 3-step filtration processes.
Coagulant for chromium neutralization was generated by 4 generators using iron shavings.	Two coagulant generators are used instead of 4 old ones.
The wastewater treatment plant occupied a 4-story building (1090 m^2). Process execution in the multi-story building required large quantities of pipes of various diameters and valves.	In order to vacate space for production processes, the treatment plant was moved to other premises with total area of 200 m^2. Yearly pipe maintenance expenses were eliminated.
Electrical consumption of the old water treatment plant was 550 kWh.	Electrical consumption of the new water treatment plant was reduced by up to 40 kWh.
Pure alkali was used for metal sedimentation. Besides, steam was used for dissolving alkali.	Alkaline solutions from electroplating processes are re-used for metal sedimentation in wastewater treatment.

Environmental evaluation

The comparison of treated wastewater quality is presented in Fig. 4. Economical evaluation of the project is characterized by the following: (i) total project cost - 290,000 EUR (including NEFCO loan of 243,000 EUR), (ii) yearly cost saving: in 1999 (3 months)-9,000 EUR; in 2000-83,000 EUR; in 2001-85,500 EUR; in 2002-86,500 EUR, (iii) Environmental savings constitutes forty percent of the total cost saving, (iv) Real payback was received in 3.4 years.

MODERNIZATION OF THE GALVANIZATION TECHNOLOGICAL PROCESS AND THE WASTEWATER TREATMENT PLANT AT JSC “VINGRIAI”

Project description

The company had the following electrochemical processes: treatment of aluminum; electroplating with chromium, zinc, cadmium and nickel and oxidation. The electroplating technology, galvanic baths and galvanic wastewater treatment equipment were obsolete and worn out. Therefore, the company inefficiently used all types of energy, raw and additional materials. Additionally, it was not environmentally feasible to use the old electrochemical equipment for metal coating with zinc, nickel or cadmium or the old wastewater treatment technology.

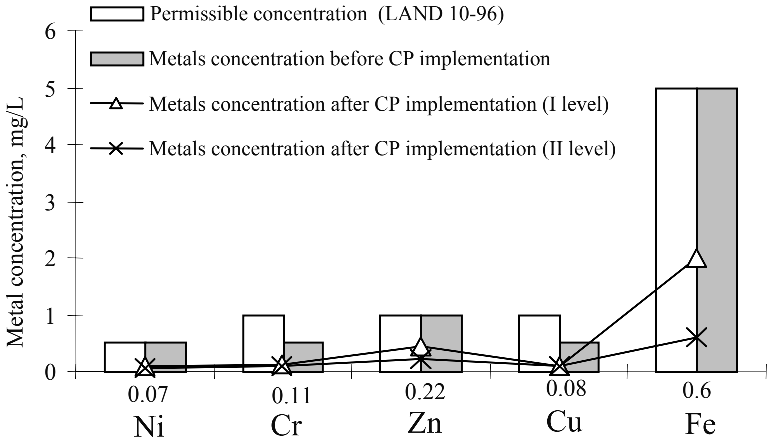

Figure 4. Reduction of metal concentration in galvanic wastewater due to implementation of new technology.

The company employed the following measures to solve its environmental problems:

(i) Reconstruction of ventilation and lighting systems in the galvanic department

(ii) Implementation of new electrochemical metal burnish and phosphotation technology instead of coating by zinc, nickel or cadmium. Wastewater volume was decreased by 33%, and wastewater quality improved

Table3. Environmental performance and monitoring method.

Environmental sector	Real benefits (2002)	Method for evaluation
Electricity saving	294,500 kWh (72%)	Electricity meter
Steam saving	10.12 MWh (100%)	Proportion of alkali saving
Compressed air saving	368,000 m^3 (88%)	Theoretical engineering calculation method
Hot water	127 m^3 (100%)	Water meter
Chemical savings (HCl, NaCl, alkali)	5.3 t (67%)	Chemical dosage system
Other material savings (quartz sand, steel shavings)	12 t (75%)	Quartz sand is not used in the new process; 50 kg of steel shavings are used for one cassette
Less sludge	7 t (13,5 %)	Sludge is supplied to the special tanks with mass indication
Heat saving for heating premises	184 MWh	Heat meter and theoretical calculation

(iii) Implementation of a new automatic electroplating process control system
(iv) Modernization of the wastewater treatment plant
(v) Recycling of 70% of the treated wastewater to the electroplating technological processes and for equipment cooling

Modernization of the wastewater treatment process was conducted though the following actions:
(i) The concentrates were collected in the different reservoirs and supplied to the main reactor using an automatic dosage system
(ii) Galvanic wastewater was supplied directly to the reactor
(iii) Metal plates were used for coagulant production
(iv) Sludge was dehydrated by a press filter
(v) An automatic pH control system was installed.

Environmental evaluation

The comparison of environmental indices before and after CP project implementation is presented in Tables 4 and 5.

Economic evaluation of the project is characterized by the following:

(i) The projects real investments were about 300,000 EUR (including NEFCO's loan of 200,000 EUR).
(ii) Cost savings – 162,000 EUR/year.
(iii) Planned payback period is about 2 years.
(iv) The cost of treatment of galvanic wastewater was decreased by more than 60%.

Table 4. Environmental effect (summary table).

	Pre-project Units/year	**Post-project Units/year (2002)**	**Savings Units/year**
Total volume of metal coated:	32,768 m^2	12,030 m^2	
Volume of wastewater after the galvanizing process	6,000 m^2	2,370 m^3	
Environmental indices:			
Electricity consumption, kWh/year	1.98 GWh	0.54 GWh	1.44 GWh
Compressed air consumption, m^3/year	254,971	38,463	216,508
Hot water consumption, m^3/year	2,270.4	29.5	2,240.9
Cold water consumption, m^3/year	21,414	995.4	20,418.6
Chemicals (alkalis, acids, salts, liquid glass), kg/year	24,851	10,010	14,841
Wastes (sludge, filtering materials, iron), kg/year	5,785	2,187	3,598
Indirect effect from electricity saving, t CO_2 /year	1,704	465	1,239 t
Minimization of metal concentration in the wastewater	38.8 kg	3.6 kg	35.2 kg

CONCLUSIONS

Optimization of galvanic wastewater treatment processes by implementation of various CP measures allows improvement of environmental performance in metal finishing companies: electricity

Table 5. The results of the environmental analysis of the galvanic wastewater and air emissions after CP implementation.

Me and pH	Concentrations in wastewater after the galvanizing process, mg/L	Concentrations after the treatment process, mg/L	Air emissions from electroplating department after modernization of ventilation system, t/year	
Cu	2.0	0.05	NaOH	0.011
Cr	25.0	0.30	Na_2CO_3	0.004
Zn	7.0	0.22	Na_3PO_4	0.004
Fe	10.0	3.00	HCl	0.002
pH	9.5	7.80	H_2SO_4	0.049
			Cr anhydrides	0.0002

consumption could be decreased up to 72%, consumption of chemical materials and sludge generation could be reduced up to 67% and up to 30%, respectively, the quality of the wastewater treatment process is significantly improved.

These results have a direct impact on the production costs. For example, it was estimated that the cost of the wastewater treatment process at JSC "Vilniaus Vingis" decreased by approximately 50%. At the same time, the product became more competitive on the market. New contracts on metal finishing have been signed after the modernized wastewater treatment plant started to operate. These contracts increased the productivity of the galvanic department by 1.5 times. Implementation of new environmentally more benign electroplating technologies in JSC "Vingriai" created opportunities to find new customers and extend the company's activity.

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EFFICIENCY OF NITRIFICATION AND DENITRIFICATION PROCESSES IN WASTE WATER TREATMENT PLANTS

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ABSTRACT

The paper deals with the factors affecting the processes of nitrification and denitrification in wastewater treatment plants. The factors are e.g. sludge age, sludge load, retention period, temperature, pH, etc. The differences in efficiency of the nitrification and denitrification processes and energy demand are compared for a variety of types of wastewater treatment plant.

INTRODUCTION

The admission of the Czech Republic into the EU necessitates the introduction of a higher standard of environmental protection into the legal system. The projects focused on technology improvement of wastewater treatment plants are the most important parts of the measures taken in order to improve the quality of the environment. The main requirement is to remove organic pollution being expressed as biological oxygen demand in five days (BOD_5) and, currently, to remove pollution mainly caused by various forms of nitrogen and phosphorus.

The aim of the paper is to assess the effectiveness of the processes of nitrification and denitrification in selected wastewater treatment plants, investigate the operational parameters of the process and identify factors, by which the process is affected.

A. Omelchenko et al (eds.),
Modern Tools and Methods of Water Treatment for Improving Living Standards, 209–217.

THEORETICAL PART

Activation is the oldest continuous cultivation of microorganisms in unsterile conditions. The technology consists of a biological unit and a separation unit. Wastewater runs into an activation tank where it is mixed with recirculated activated sludge. The mixture is intensively aerated. Finally the sludge is separated from cleaned water. Concentrated activated sludge is returned back to the activation tank. It is necessary to periodically remove surplus activated sludge.

The requirement to remove nutrients, i.e. nitrogen and phosphorus compounds, from cleaned communal waste waters, has gradually been introduced into the legal water regulations of the Czech Republic since the 1970s and the standards have been increased up to the present level (Government Regulation 2003). The increased occurrence of nutrients in the discharged wastewaters can cause the following problems to recipients: (i) toxic impact of ammonia (mainly its undissociated form) on water microorganisms, (ii) eutrophication of surface waters, (iii) increased concentration of nitrates and consequently nitrites in drinking water, and (iv) increased expense of water treatment in the water supply system.

Through the classic activation process the concentration of nitrogen contamination in wastewater is reduced only by its consumption for the creation of new biomass. The increasing concentration of nitrogen substances in wastewaters resulted in the need for a gradual introduction of the second, biological level, which consists of nitrification and denitrification. The classic activation process is supplemented by this level at the present time.

Ammonia nitrogen is oxidised to nitrites and then on to nitrates during nitrification. Nitrification is an aerobic process. The oxygen concentration in a tank should not drop under 0.5 mg/L (the recommended value is ca 2 mg/L). The redox potential is higher than 50 mV. Denitrification is an anoxic process in the presence of nitrites, nitrates and a minimum concentration of dissolved oxygen. Nitrates and nitrites are the sources of oxygen for microorganisms. Nitrates generated through nitrification are reduced up to nitrogen gas during denitrification. The concentration of dissolved oxygen should not exceed 0.5 mg/L. The redox potential varies from -50 to 50 mV. The optimal pH level for both processes is ca 7.5.

The occurrence of organic carbon, which is a substrate for the creation of new biomass, is also necessary in the process of denitrification. It is possible to reach more than 90% efficiency in removing nitrogen from wastewaters in optimal working systems.

RESULTS AND DISCUSSION

The metabolism of nitrifying bacteria is sophisticated and characterised by its low energy yield. Therefore the nitrifying bacteria have a low specific growth rate and they are affected by a number of inhibitions. An important parameter having an impact on the nitrogen removal effectiveness is the sludge age, i.e. the average time period during which sludge remains in the biological system. If the sludge age is lower than the generation time of nitrifiers, they will be washed out of the system and it will not be possible to have efficient nitrification (Konecny 1980, Chudoba 1991). If the removal of nitrogen contamination is to be efficient, the total time during which the wastewaters are kept in the activation tank must be longer than the time calculated for nitrification.

The sludge load is another relevant factor affecting the efficiency of the process. The load is defined as the weight ratio of removed substrate to a kilogram of dried activated sludge per day. The category of activation according to sludge load and age is shown in Table 1 and corresponds with the data commonly noted in the literature (Maly and Mala 1996).

Table 1. The category of activation according to sludge load and age.

Activation	Sludge age, d	Sludge load according to BOD_5, kg $kg^{-1}d^{-1}$	Retention period of wastewater in activation tank, h
Low load	> 25	0.05 – 0.1	24 – 72
Medium load	3 – 15	0.2 – 0.5	4 – 12
High load	< 3	> 1.0	1 - 2

The categories shown above are approximate and there are no sharp boundaries between the individual systems. In the case of medium and low loads of activation the cleaning effect is over 90 % as measured by BOD_5. The fundamental difference between the wastewater treatment systems is not in the level of elimination of the natural organic run-off contamination, but mainly in the quality of the excess sludge being produced. The sludge is stable and can be transported from wastewater treatment plants in the case of low load of the systems where the sludge age is $t_{sa} > 25$. On the other hand in the case of medium and especially high load plants the sludge is not stable and it must be stabilised prior to further treatment. In case of high load of the systems it is also necessary to take into account the gradual decrease of cleaning efficiency (70-80 % according to BOD_5) and the collapse of the whole process in case a certain limit of load is exceeded.

As denitrification bacteria require the presence of an organic substrate as a source of carbon and energy it is necessary in the case of a shortage of natural substrate to add a source of organic carbon, which could be used by bacteria with high efficiency. The substrate and its metabolic products should meet certain basic standards. It must not be toxic, the BOD_5 /COD (chemical oxygen demand) ratio must be higher than 0.6 and the BOD_5 must be larger than 10^4 mg/L (Bilanin 1995).

The municipal wastewater treatment plants are operated in such a way that part of the BOD_5 in the inflow is taken directly into the denitrification tank. It is necessary to have 2-3 g organic substance as measured by BOD_5 to remove one gram of nitrogen in the form of nitrates, depending on the composition of the wastewater.

Regulation of the oxygen supply according to actual requirement contributes to a reduction of the energy demand of the aeration systems. The concentration of dissolved oxygen is the simplest and the most frequently used variable for regulation of the activation air input. The determination of redox potential is suitable for measuring oxygen activity. Redox potential is one measure, which informs on the progress of biological processes of wastewater treatment. The value of redox potential relates to the type of oxidation-reduction reactions and the environment in which they take place.

It is extremely difficult to recommend the most suitable technology and the method of nitrogen removal in municipal wastewater treatment plants. In the early days of the use of activation for biological nitrification and denitrification so called two or three-sludge systems were introduced. Biocenoses responsible for oxidation of organic pollution, nitrification and denitrification were separated in the systems. The use of one-sludge systems is the result of further development. In this case the activated sludge contains both an organo-trophic population (an aerobic and anoxic denitrification one) and a nitrification population of microorganisms. Preliminary denitrification, (pre-denitrification), simultaneous nitrification and denitrification and the postponed denitrification (post-denitrification) are included in the basic layout scheme for the removal of nitrogen.

Pre-denitrification is the system in which a denitrification reactor is placed first and influent wastewater is mixed with active sludge under anoxic conditions and thus provides the source of organic nitrogen for denitrification. Part of the nitrified output (nitrates) from the second aeration tank is returned to the denitrification stage.

Simultaneous denitrification is a compromise between pre-denitrification and postdenitrification. Aerobic and anoxic processes are alternating within one reactor. It can be carried out in two different ways: (i) change of aerobic and anoxic zones (spatial segregation) and change of aerobic and anoxic periods (time segregation).

Post-denitrification is the only process, which is able to eliminate nitrogen completely. A major part of wastewater BOD_5 is removed inside an aerobic tank while the endogenous denitrification occurs mainly inside an anoxic tank. The anoxic process is usually very slow and it requires a high retention period and a large volume tank.

The efficiency of nitrification and denitrification processes was monitored in three wastewater treatment plants for dependence on various factors. The wastewater treatment plants differ in the level of activated sludge load, the technology of purification and also in the number of equivalent inhabitants served by the system.

The first, a high load wastewater treatment plant I_a (situated in Vyskov, Czech Republic) started operation in 1977. It was a mechanical-biological wastewater treatment plant with anaerobic stabilisation of excessive sludge. The reaction volumes of the biological part were dimensioned only for the removal of BOD_5. The plant was not able to remove nutrients with the required efficiency. That is why reconstruction was started in 2001 and the plant started its trial operation in mid-2002.

In this way a low load mechanical-biological wastewater treatment plant I_b (current facility in Vyskov, Czech Republic) came into existence. It has got anaerobic stabilisation of sludge and it is able to remove nitrogen and phosphorus efficiently. Activation is low load with a long sludge age and it is ideal for a high level of nitrification and denitrification. The process of nitrification and denitrification is carried out by creating aerobic and anoxic zones inside the activated sludge unit (spatial segregation). The whole technological process is controlled by an automated control and monitoring system. New activations are operated either in an interrupted nitrification-denitrification regime, when aerobic phases with aeration interchange with anoxic phases only with mixing, or they are carried out in the regime of permanent aeration, when the concentration of dissolved oxygen is maintained at a level of about 2 mg/L. The schematic of the activation tank, where the nitrification and denitrification is carried out, is apparent from Fig. 1. In Fig. 2, this activation tank is presented in reality. The inlet and technological parameters of the reconstructed wastewater treatment plant is presented in Tables 2 and 3 respectively. Only 38,330 equivalent inhabitants are attached to this facility. Last year the treatment plant removed 630,424,200 t of organic pollution from wastewater as measured by BOD_5. The total electric power consumption was 630,074 kWh. The wastewater throughput was almost constant in individual months of the year and the total annual amount was 2,537,454 m^3. Measurements in the newly reconstructed circulation activation tank showed that the wastewater treatment plant I_b has suitable conditions for nitrification and following denitrification (see Table 4). Another low load waste water treatment plant II (current facility in Prostejov, Czech Republic) being assessed is a mechanical-biological one with the removal of nutrients, anaerobic sludge stabilisation by mesophilic digestion and water removal on a centrifuge. The activation reactor operates discontinuously with aeration and non-aeration periods, which are cyclically repeated (time segregation). The activation process takes place in four activation tanks. Individual reactors are filled in turn and then the treatment process takes place in its individual phases. Each reactor is aerated for half of the whole cycle as a maximum. The inlet and outlet parameters of the observed wastewater treatment plant are shown in Tables 2 and 4. One of the activation tanks of the facility described is shown in Fig. 3.

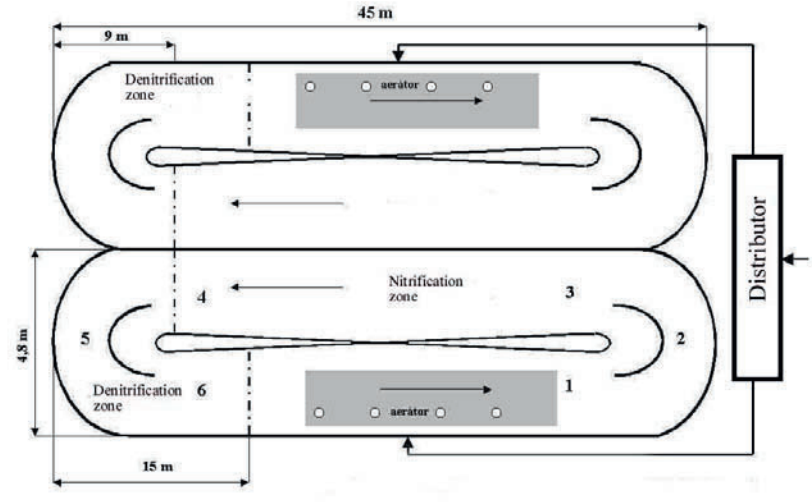

Figure 1. Scheme of the activation tank of wastewater treatment plant I_b. The numbers indicate the places of sampling.

Figure 2. The activation tank of wastewater treatment plant I_b.

Table 2. Comparison of inlet parameters of wastewater treatment plants (WWTP) I_b and II.

Inlet Parameter	Symbol	Unit	WWTP I_b	WWTP II
Number of equivalent inhabitants	EI	--	38330	110300
Average daily inlet	Q_{24}	$m^3\ d^{-1}$	9000	21500
Maximum rain inlet to WWTP	Q_{max}	$m^3\ h^{-1}$	450	1300
Maximum rain inlet to activation	$Q_{max.B}$	$m^3\ h^{-1}$	792	1800
Organic pollution	BOD_5	$kg\ d^{-1}$	2300	6500
		mg/L	256	350
	COD	$kg\ d^{-1}$	5000	14200
		mg/L	556	660
Undissolved substances	US	$kg\ d^{-1}$	2100	4400
		mg/L	233	250
Total nitrogen	N_t	$kg\ d^{-1}$	402	1100
		mg/L	45	50
Total phosphorus	P_t	$kg\ d^{-1}$	100	150
		mg/L	11	6

Table 3. Basic technological parameters of the wastewater treatment plant I_b.

Technological parameter	Desired value	Average value taken
Temperature	> 12°C	15.4 °C
Concentration of oxygen in nitrification phase	1.5 – 2 mg/L	1.96 mg/L
Concentration of oxygen in denitrification phase	< 0.5 mg/L	0.29 mg/L
pH	6.5 – 8	7.46
Sludge age	10 – 30 d	20 d

Table 4. Outlet parameters of wastewater treatment plants (WWTP).

Outlet parameter	Unit	WWTP I_a	WWTP I_b	WWTP II
Removal of BOD_5	%	90	94	98
Removal of undissolved substances	%	85	93	97
Efficiency of nitrification	%	28	85	95
Efficiency of denitrification	%	21	62	80

Figure 2. The activation tank of wastewater treatment plant II.

Table 5. Comparison of the energy demand of treatment process technologies.

Parameter	Values of WWTP Ib	Values of WWTP II
Total consumption of energy [kWh]	630,074	2,609,429
Specific consumption of energy per m^3 of wastewater [kWh m^{-3}]	0.2483	0.4556
Specific consumption of energy per equivalent inhabitant [kWh EI^{-1} $year^{-1}$]	16.44	23.66
Energy consumed in the removal of one ton of BOD_5 index [kWh t^{-1}]	0.925	2.004

The aim of the reconstruction and modernisation of wastewater treatment plant I_a was to increase the efficiency of purification and the quality of treated wastewaters with minimal environmental impact and cost. It was proved that the efficiency of treatment in relation to BOD_5 increased from an initial 90 % to 94 %. The efficiency of nitrification increased from 28 % to 85 % and denitrification from 21 % to 62 %. It is clear that the technology of the wastewater treatment plant II is of a higher quality when compared with the wastewater treatment plant I_b; the efficiency of nitrification is higher by 10 % and denitrification by 18 %. On the other hand the electric power demand is four times higher due to the technological process being used. The technology being used in the wastewater treatment plant I_b has a significant advantage in lower costs per equivalent inhabitant and per ton of organic pollution BOD_5.

The environmental burden is approximately the same as determined by Life Cycle Assessment. In the case of wastewater treatment plant II the direct load of surface waters is reduced, however the environmental burden is higher due to higher consumption of electric energy.

CONCLUSIONS

It was proved that the wastewater treatment plant with standard high-load technology provides a sufficient reduction of BOD_5, but it does not remove all the nutrients. By comparison with low-load wastewater treatment plants with simultaneous denitrification it was proved that: (i) the efficiency of BOD_5 reduction is sufficient and (ii) the removal of nitrogen substances through the technologies of both spatial and time segregations is sufficient as well.

The above-mentioned conclusions are true in case the required parameters of substrate, quality and sufficient age of sludge and other operating conditions are met. The technology of alternating anoxic and aerobic zones has rather lower process efficiency, on the other hand there is significantly less energy demand and therefore less expense.

The removal of phosphorus was not monitored in the wastewater treatment plants discussed and it is the subject of current research.

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ELECTROCHEMICAL PROCESSES FOR WASTEWATER PURIFICATION UTILIZING FLUIDISED BEDS OF PARTICLES WITH DIFFERENT CONDUCTIVITY

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ABSTRACT

Some fundamentals and applications of electrochemical systems containing 3–dimensional electrode systems with dynamic matrix, fluidized beds, consisting of particles possessing different conductivity, namely: non-conductive (glass or plastics), conductive (metal granules), semi-conductive (various carbon materials) and ion conductive (ion exchangers) are discussed. The principles of control of electrochemical processes in particulate beds are formulated. The advantages of the fluidised beds are demonstrated by application to water management.

INTRODUCTION

The primary goal of any environmentally benign technology is to eliminate the pollutants at the place of their formation. In this regard, chemical-free technologies and, particularly, electrochemical technologies offer enticing opportunities. From our experience, electrochemical systems, which use 3-dimensional (3-D) electrodes, are very effective in removing various types of contamination from potable and wastewater.

The fluidized bed electrochemical reactors (FBER) are attractive in terms of their capacity and operability in many fields of electrochemical technology, especially in the treatment of dilute or complex solutions (Marshall and Walsh 1985).

A. Omelchenko et al (eds.),
Modern Tools and Methods of Water Treatment for Improving Living Standards, 219–234.

Their advantages consist of high specific area of electrode surface, elevated heat- and mass-transfer rates, usage of granulated materials known in a variety of branches of chemical technology, simplicity of automation, etc. The interior space of an electrochemical reactor is used in the optimum way. Schematically, the advantages of FBER are demonstrated in Fig. 1.

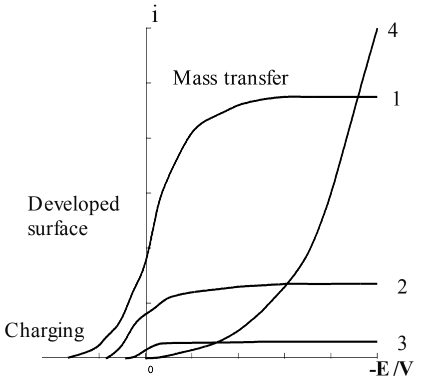


Figure 1. The concentration changes during the extraction of reagent on the 3-D electrode. 1-3 - partial curves of electroreduction of metal ions, $c_1 > c_2 > c_3$; 4 – partial curve of hydrogen reduction.

They allow the enhancement of mass transfer due to intensive stirring and collisions and usage of the whole reactor volume for electrochemical reaction. They also make possible surface charge control of the processes in reactors with a large electrode area. These factors work against domination of hydrogen evolution, which impairs the efficiency of electrolysis.

The current work represents the family of FBER, which have been extensively studied and used for treatment of dilute solutions. Such reactors use the following particles: (i) non-conducting (glass, sand or plastics), (ii) conducting (metal or metal-coated granules), (iii) semiconductor (various carbon materials), and (iv) ion conductive (ion-exchange resins or inorganic ion exchangers). Each type of fluidized bed electrochemical reactor is suitable for the treatment of dilute waste and multicomponent solutions by means of electrolysis, electrosynthesis, electrochemically-controlled adsorption, and ion-exchange.

The objective of this study was to compare the electrochemical characteristics of various fluidized bed systems, to find similarities and distinctions in electrochemical behavior, and to define the main fields and limitations of their use.

Schematically, the fluidized bed electrode is represented in Fig. 2.

Configuration (a) is mainly used in laboratory practice, whereas configuration (b) is employed in commercial electrochemical reactors (Marshall and Walsh 1985).

The 3-D electrode system is known to be rather complicated, as the distribution of polarization has to be taken into account (Todes and Tsitovich 1981, Shvab et al. 1983). Such distribution leads to non-uniformity of reaction rates inside the bed and provides high selectivity of electrochemical reaction. Along with electrochemical parameters, the hydrodynamics should be taken into account for successful design of the reactor, since the intensity of electrode processes is mainly determined by the dynamics of fluidization.

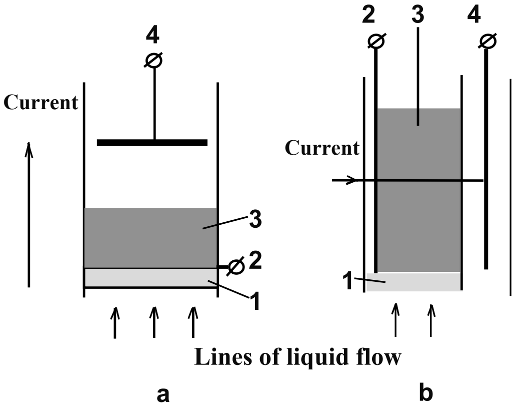


Figure 2. FBE configurations: (a). Parallel arrangement of electric current and liquid flow, and (b) perpendicular arrangement of electric current and liquid flow. 1-flow pre-distributor, 2-current collector, 3-3-D-electrode bed, 4-counter electrode.

HYDRAULIC STRUCTURE OF THE FLUIDIZED BED ELECTROCHEMICAL SYSTEM

The character of particle movement in the fluidized bed (FB) is determined by the regime of fluidization. In ideal conditions, a uniform regime of fluidization is realized. The system represents so-called pseudo-homogeneous structure (Todes and Tsitovich 1981). Particles of a FB are in random motion. The velocities of this motion do not exceed the average flow rate of a fluidizing agent, the so-called constrained flow rate, U_{in}, although instantaneous flow rates between separate FB particles can be much higher. Shvab has shown (Shvab et al. 1983), that U_{in} is practically constant within a FB, whereas flow rates outside the bed are much higher and do not depend on it.

Particles of various sizes are fluidized at different flow rates. Therefore, in polydispersed systems, separation of particles takes place; with larger particles gathering at the bottom of the bed. For fluidization of such systems V-form apparatus is used (Romankov and Rashkovska 1964).

The movement of particles in a stream results in collisions with each other and with the walls of the apparatus. As a result of the basic instability of uniform distribution of particles in the reactor volume, fluctuations of porosity occur in the bed (Romankov and Rashkovska 1964). Areas with increased porosity (bubbles) and with lowered porosity (packages of particles) are produced. The former rise upwards, whereas the latter move downward initiating chaotic oscillations of the vertical component of the vector U_p, where U_p is the direction of particle movement. The FB is more or less homogeneous at flow rates slightly exceeding U_{mf}, where U_{mf} is the minimum fluidization velocity to agitate the bed (Romankov and Rashkovska 1964). However, at elevated flow rates and increased porosity, some bubbles, packages and channels could be formed.

In chemical reactors, application of uniform fluidization is important to maintain a proper contact between the electrode and the distributor-current collector as it protects the distributor from abrasive and thermal action of the particles in the stream (Gorodysky et al. 1980, Shvab et al. 1980) and, at the same time, maintains effective electrochemical reaction. To promote contact, different hydraulic systems with circulating beds were proposed (Kazdobin et al. 2000). The design of the flow pre-distributor, which allows variable hydrodynamic resistance, provides an efficient electrochemical reactor for particles of different density.

REACTORS WITH FLUIDIZED BEDS OF NON-CONDUCTING BEADS

Reactors with fluidized beds of non-conducting (glass) beads or fluidized bed electrolyte reactors are used for recovery of metal ions from dilute and concentrated effluents from electroplating plants. They allow recovery of about 99% of metals, which are commonly used for electroplating, except chromium. For example, electrolysis in such fluidized inert beds (FIB) was successfully applied for extraction of non-ferrous and noble metal electroplating wastes (BEWT 1985, OAO “Temp” 2003). In addition, units with FIB provide more than ten-fold reduction of rinse water, reuse of smooth metal deposits as anodes in the electroplating bath and significant decrease of the toxicity of wastes.

The use of FIB (Le Goff et al. 1969), in which the solid phase usually consists of spherical glass particles, is one of the most efficient methods of disturbance of the diffusion boundary layer to enhance mass transfer.

To determine the contribution of hydrodynamics in electrochemical processes, the effect of particle-wall collision on the mechanism of mass transfer in liquid fluidised bed cells has been studied (Shvab et al. 2000a, b). Calculations of the contribution of the particle collision mechanism to total mass transfer have shown that in beds consisting of particles with low density

(ρ_p) the contribution of collision currents dominates, and in beds of particles of greater dencity it is small (Fig. 3).

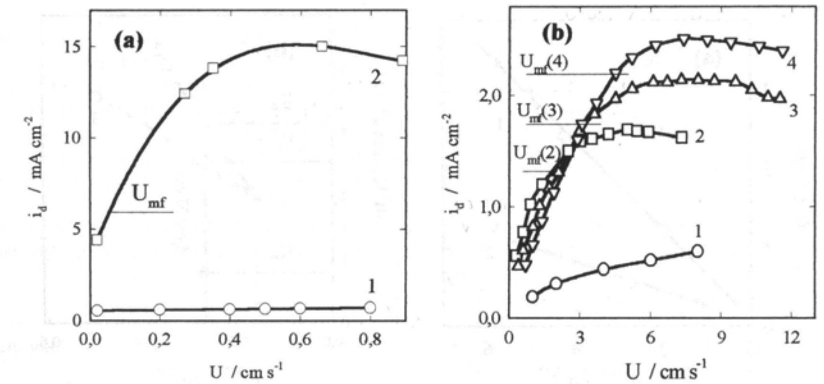


Figure 3. Dependence of limited current of Cu^{2+} reduction on electrolyte flow rate in a flow without particles (1) and in a FIB of particles with different density. (a) Granulated ion-exchange resin KB-4. 2 Diameter of particles d_p = 0.07 cm; ρ_p = 1.25 g cm^{-3}. b - Copper granules; for lines 2, 3, and 4, d_p = 0.055, 0.090, and 0.125 cm; respectively; ρ_p = 8,9 g cm^{-3}. Electrolyte (in M): (a): 0.1 Cu^{2+}, 0.75 Na_2SO_4, pH 3; (b): 3.15 mM Cu^{2+}, 1 Na_2SO_4; pH 2.5.

By selection of particle size and density, it is possible to vary the contributions of flow rate and particle collisions to the mass transfer, and, thus to estimate the contribution of hydrodynamics to electrochemical processes, which is necessary for the design of reactors.

The determination of the mass transfer input confirmed the advantages of fluidization of relatively “light” particles, such as carbon and ion exchange materials.

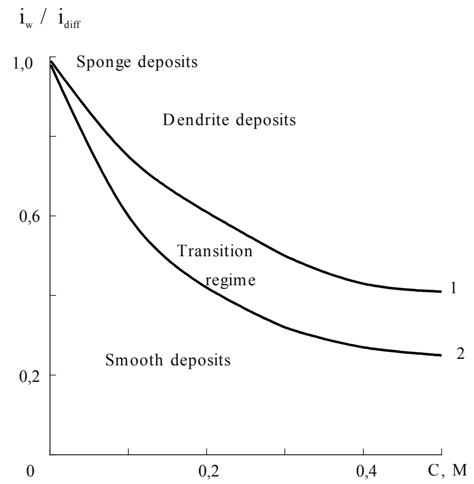


Figure 4. Dependence of quality of metal cathodic deposits in FIB on concentration of metal ions and relative working density of a current, i_w/i_{diff}. 1 - Ni, Co, Pd; 2 - Cd, Pb, Ag, Au; transition area - Zn, Cu. Average particle diameter 0.09 cm. Relative bed expansion L = H/H$_o$ = 1.5, where H is the height of fluidized bed, H$_o$ is the height of static bed.

Based on the mass transfer characteristics detected, the regimes of metals deposition in FIB from solutions of different concentration were determined (Fig. 4). They allowed design of the technology for recycling of rinse water in the electroplating industry.

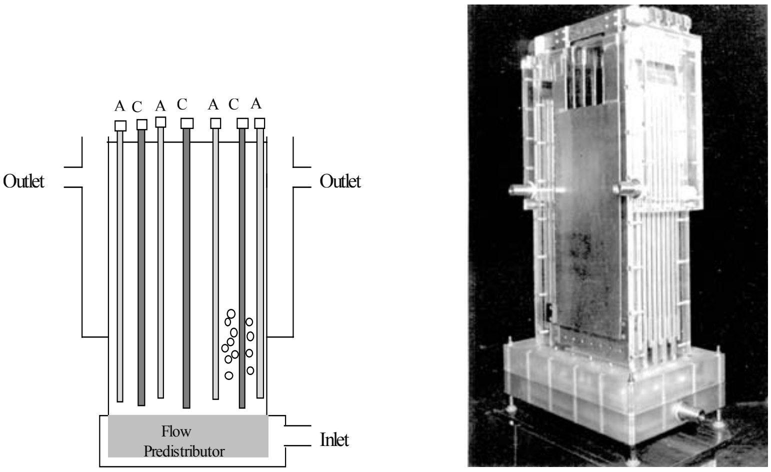


Figure 5. Electrochemical cell arrangement with fluidized beds of non-conducting (*Ballotini* glass) beads.

The corresponding cell arrangement is shown in Fig. 5 and technical characteristics are presented in Tables 1 and 2.

Table 1. Technical characteristics of the FIB cell with maximum current 500 A.

Extracted metal	Cu	Cd	Ni	Zn	Sn	Ag	Au
Capacity, kg/h	0.4	0.9	0.45	0.45	0.9	1.9	3.5
Residual concentration, mg/L	0.5-1	1-5	5	15	2-5	0.5	0.5
Average current efficiency, %	85	80	45	50	60	65	65
Time of treatment of 1 m^3 of solution	80	70	175	36	32	30	40

Table 2. Capacity of the cell depending on concentration.

Concentration of metal ions, g/L	Quantity of electrodeposited metal, g m^{-2} h^{-1}					
	Cu	Cd	Zn	Ni	Ag	Au
1	65	50	46	40	105	190
0.1	5.3	4.5	4.2	3.8	11.0	18.0
0.01	0.35	0.24	0.08	0.10	1.0	1.5
0.001	0.02	0.02	-	-	0.08	0.12

This technology is commercialized and reactors with non-conducting particles are installed at electroplating plants in the City of Khmel'nitski, Ukraine (OAO “Temp”2003). Electrolysis in FIB can be considered as a useful but auxiliary technology in waste treatment. It allows elimination of the most hazardous wastes and purification of relatively concentrated effluents including those originating from ion exchange devices.

FLUIDIZED BED ELECTRODE (FBE) REACTORS

Fluidized bed electrode (FBE) reactors are of great and permanent industrial interest (Marshall and Walsh 1985). In general, they have unique technological characteristics. However, one negative feature showing up in the application of such systems should be noted. During development of methods of ion extraction down to minimum residual concentration, it is necessary to take into account collateral reduction of dissolved oxygen. Its concentration in solutions reaches 5.8×10^{-4} M, whereas, for example, metal ions are often to be winned down to a concentration about 10^{-6} M. Due to this, a lot of attempts to apply FBE directly to metal ion winning from dilute wastes have failed as a result of extremely low current efficiency.

Our experience shows that FBE is applicable for metal electrowinning, separation, and refining in hydrometallurgy, high purification of electrolytes, and electrosynthesis. High purification of electrolytes allows replacement of existing chemical methods of electrolyte conditioning in different areas of metal finishing with chemicals-free electrochemical treatment. A family of FBE reactors has been designed in our laboratory (Shvab et al. 1980). Schematically, the construction of FBE reactors is presented in Fig. 6.

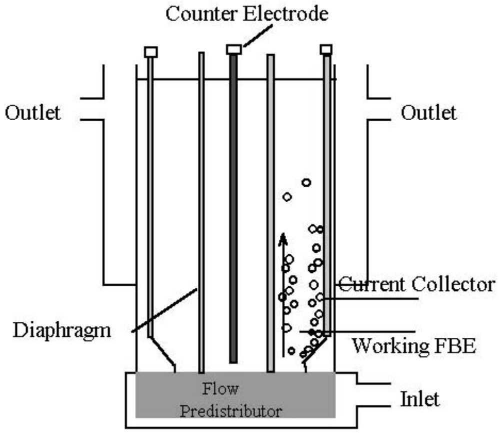


Figure 6. Fluidized bed electrode cell arrangement.

The advantages of our design are as follows: (i) the original FBE asymmetric reactor arrangement, (ii) controlled polarization profiles of the discontinuous metal electrode phase, and (iii) non-polarized electrode current collector. The FBE reactors designed in our laboratory were tested in long-term trials on a pilot-plant scale in the processes of Cu, Ag & Au electrowinning, Cu-Ni, Cu-Cd, Pb-Ni, Cu-Zn separation, Ni electrochemical refining, and electrosynthesis of some drugs. Particularly, the FBE pilot reactors were installed in Noril'sk and Severonickel metallurgical plants in Russia, and in several other electroplating plants for metal ion electrowinning from dilute effluents.

Another prospective application of FBE is thought to be for technological processes based on the charge control of the electrode surface. One of them is the electrochemically-controlled sorption-desorption (electrosorption) of organic molecules in dynamic beds of carbon materials. To control adsorption and ion exchange of substances, either ionic or molecular, on carbon materials, the structure of the interfacial double electric layer (DEL) and/or sign and value of the interface charge should be changed. According to the theory of electrochemically controlled adsorption or electrosorption (Frumkin 1982, Grevillot 1989, Golub et al. 1987, Alkire and

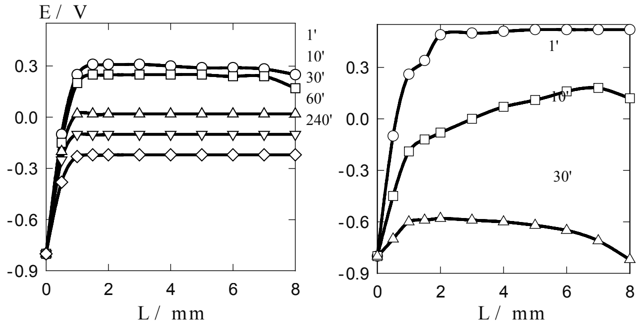
Eisinger 1983, Mayne and Shackleton 1985, Woodard and Jansson 1986), the adsorption of negative particles will preferentially take place on the positively charged electrode surface, and, conversely, the positive particles will better interact with negatively charged electrodes. At the same time, the adsorption of neutral particles of molecular structure on an electrically neutral surface, at the so-called potential of zero charge (Frumkin 1982), will be enhanced.

In the case of porous carbon materials, the use of electrosorption has certain limitations, which decrease the efficiency of such electrodes. One of these limitations is that the DEL formation is minimal in micropores. Also, the efficiency of the regeneration process is determined by the porous structure of the carbon adsorbent. According to Khabalov et al. (1989), only mezoporous adsorbents can be used for electrochemical regeneration.

To gain insight into the applicability of porous carbon materials for removal of organic species from water by electrosorption, we studied the electrochemical properties of synthetic carbon granules (Kazdobin et al. 1996). This study was based on the Frumkin theory of electrochemical sorption in three-dimensional particulate systems. The kinetics of electrode potential formation in fluidised particulate beds of carbon materials with semiconductive properties was studied by the collision method proposed in (Gorodysky et al. 1980). The development of π-polyconjugation chains, depending on the composition of the initial materials, the presence of heteroatoms (electron donors or acceptors), non-carbon impurities, and the temperature of synthesis, was taken into account. The investigation has shown the influence of the carbon matrix structure on the rate of oxygen chemisorption and consequent processes of adsorption, ion exchange and electrocatalytic transformations of adsorbed matter. This study resulted in classification of carbon materials based on the extent of carbon matrix regularities, which allows the assessment and forecasting of the properties of the electrodes and sorption materials produced.

As an example, the electrosorption of typical organic pollutants, such as benzoic acid, phenol, and chloroform may be described. Usually, the application of electrosorption using carbon electrodes is considered as inefficient (Grevillot 1989). It was suggested that this is due to the non-uniform potential distribution within the bed of carbon material. Therefore, polarization profiles in the bed of carbon granules were measured (Fig. 7).
It was shown that the potential profiles depend not only on bed porosity and conductivity but also on time.

The polarization phenomena on 3-D carbon electrodes differ from that on electrodes containing metallic particles. For example, the average polarization shifts not to the current collector, but to the front of the electrode upon increasing electrolyte conductivity. This may be caused by charging of the micropores of the carbon body, which can change the structure of the double electric layer (DEL). Due to this reason, the application of current is



(a) (b)

Figure 7. Time- and length-dependent polarization profiles of carbon beds in 7 mM (a) and 80 mM (b) solution of Na_2S0_4, pH 5. The current collector is placed at the bottom of the bed.

ineffective in dilute electrolytes. The electrode potential of the carbon bed slightly changes with time, and differs from that of the current collector. In contrast, increase of electrolyte concentration makes possible control of the potential distribution within the bed.

In general, surface area and porous structure play a significant role in electrosorption. With respect to various carbon materials, the influence of

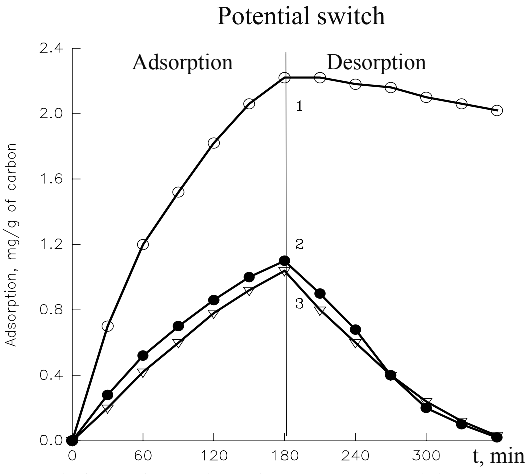


Figure 8. Adsorption and electrodesorption of $CHCl_3$ at potential -1.4 V on the microporous (1, 2) and mezoporous (3) carbon fibers. Samples: 1- charcoal SCS™, 2 and 3-carbon fibers. Specific surface $S_1 = 918\ m^2/g$, specific surface $S_{2,3} = 682\ m^2/g$.

these factors was tested during electrosorption of $CHCl_3$ on them (Fig. 8). $CHCl_3$ was extracted from a model solution of potable water containing 7 mM Na_2S0_4, pH 5. The electrodesorption was carried out from a solution containing 80 mM Na_2S0_4 at pH 5.

It can be seen from Fig. 8 that carbon materials with specific surface, S, of about 600 m^2/g and mainly mezoporous structure are efficient in electrodesorption. On microporous carbon material with a larger surface area, the rate of adsorption-desorption cannot be properly controlled electrochemically. It is also apparent that the cathodic polarization is optimal for desorption of $CHCl_3$, which is characteristic for most organic molecules. During desorption, the adsorbed hydrogen atoms displace the previously adsorbed organic molecules.

In our opinion, the method of electrosorption is promising but it is too complicated and expensive for modern use. Besides, the cell is prone to bio-fouling. Therefore, the electrosorption cells could be used in limited cases for extraction of some unique particles or in electrosynthesis. The latter may be illustrated by the production of L-cysteine for medical purposes via reduction of cystine in a medium containing sulfuric acid (Furman et al. 1992). This process is of practical interest for production of drugs, food additives, etc. The reaction runs in "mild" conditions with a small deviation of the carbon FBE potential from the stationary one.

Specifically for this novel technology, a carbon electrocatalyst was designed that has allowed essential improvement of the parameters, as compared to the technology using organo-tin regeneration, by increasing the degree of transformation of the reagent, and decreasing the environmental impact of the process. The process is conducted in sulphate solution, which permits easy separation of the products of electrolysis from the initial reagents, increases the selectivity of the process, and prevents formation of substances with high molecular weight and products of destruction. The yield of product is up to 4 g per A×h at a current efficiency up to 80 %. Experimental batches of the drug were obtained at two pharmaceutical plants in Ukraine.

ELECTROCHEMICAL REACTORS WITH BEDS OF INORGANIC ION EXCHANGE MATERIALS BASED ON TI AND ZR PHOSPHATES

Electrochemical reactors with beds of inorganic ion exchange materials based on Ti and Zr phosphates give the possibility of metal ion sorption from very dilute solutions accompanied by their electroreduction. This provides chemical-free regeneration of ion exchange materials, which are widely used in environmental protection. Such technologies may be feasible in the concentration range where traditional electrochemical technologies have low efficiency. Besides, it offers some possibilities for electroplating in two-phase electrolytes containing trace amounts of salts and ions of interest in immobilized form within the fluidized phase of the ion exchanger.

A similar process was proposed recently by General Motors Co. (Tison 1988 and 1989) but it had rather low current efficiency. In our laboratory, we found a way to sharply increase the continuous metal electrodeposition efficiency from rather dilute solutions in the presence of inorganic ion-exchangers (IEM). Some typical current-voltage curves for Cu^{2+} reduction on the electrode in the presence of a fluidized bed of ion exchanger are represented in Fig. 9.

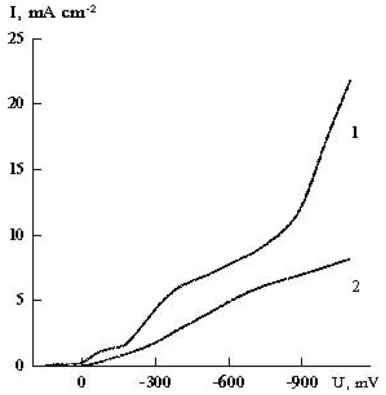


Figure 9. Current-voltage curves of Cu^{2+} electroreduction in a bed containing the ion exchanger TiPh. Relative bed expansion L = 1.3. d_p = 0.07 cm. Solution: 1 - bidistilled water, 2 - 0.01 M Na_2SO_4, pH 3.8.

The direct transfer of Cu^{2+} ions from the ion exchange phase to the electrode followed by their electroreduction was detected by current-voltage measurements. The transfer rate was found to be dependent on the bed expansion. The electrochemical reaction constants of the electrode in the presence of TiPh were as follows: exchange current i_o=3.42x10^{-5} A/cm^2, transfer coefficient α= 0.936. The current efficiencies (CE) of Cu deposition in the bed from TiPh surprisingly rise on decreasing Cu^{2+} ion concentration in the electrolyte (Fig. 10).

The Cu^{2+} concentration in the bulk ion exchanger was 100 - 1000 times larger than in the bulk electrolyte. With respect to CE, one may conclude that direct Cu^{2+} ion reduction from the solid phase is preferable. The value of α close to 1 shows that the transport of Cu^{2+} occurs practically without stripping the solvate layers. In the presence of the TiPh phase, all the energy of the double electric layer is spent on the discharge act, and the transfer of ions

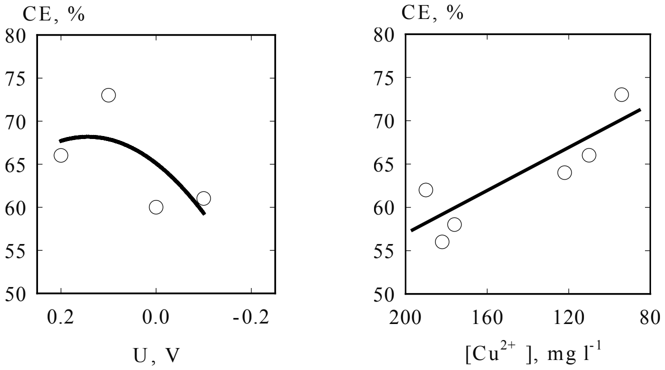


Figure 10. Dependence of current efficiencies (CE) for Cu deposition on the electrode potential, U, and concentration of Cu^{2+} ions in the electrolyte. Relative bed expansion L = 1.3. d_p = 0.07 cm. Solution: 1 - bidistilled water, 2 - 0.01 M Na_2SO_4, pH 3.8.

across the three-phase interface, ion exchanger-electrolyte-electrode occurs according to the barrier-less mechanism.

Higher values of electrode constants for inorganic ion-exchangers, as compared to organic resins (Tison 1988), provide higher working current densities (CD), which are comparable with those estimated for concentrated electrolytes. The structural analysis of Cu deposits has shown that Cu^{2+} electroreduction in the presence of TiPh occurs under activation control over a wide range of potentials, contrary to the bulk aqueous electrolytes, for which mass transfer control takes place at the same potential.

Long-term trials of the effect of continuous addition of dilute $CuSO_4$ solution into the recirculation bath were conducted. They have shown (Fig. 11) that direct high efficient electrowinning of electropositive metals from an ion exchanger is possible using fluidized beds of polarized ion exchangers. Increasing acid concentration and decreasing pH that lead to diminishing ion-exchange capacity may cause an observed decrease in CD and CE with time.

The studies conducted have confirmed the applicability of the method of direct metal ion electrowinning from dilute solutions. The advantages of employing inorganic ion-exchangers are confirmed. The simplicity of this method allows it to be recommended for post-treatment removal of metal ions from wastewater.

Based on experience gained, some recommendations may be given for the implementation of different fluidized bed systems. The comparative characteristics of fluidized bed reactors with particles of various conductivities are listed in Table 3.

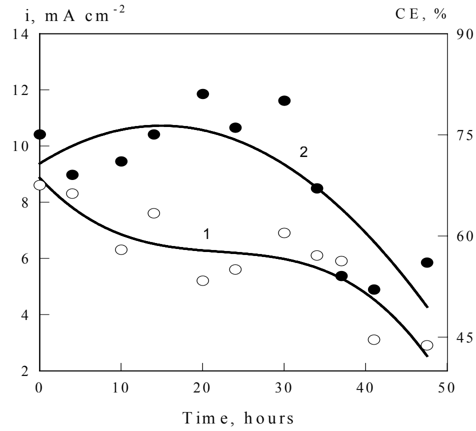


Figure 11. Time-dependence of working CD (1) and CE (2) of Cu deposition onto the electrode in the fluidized bed of TiPh ion exchanger. L = H/H_o = 1.3, d_p = 0,07 cm, pH 3.3. Ratio solid:liquid by volumes is 1:100.

Table 3. Working characteristics of fluidized bed reactors with particles having various conductivity and the main fields of their use.

Class	Concentration of reagent, M	Working CD, A/m^2	Working voltage, V	Current efficiency, %	Field of use
1	1 - 10^{-5}	300 - 5000	2 - 8	95 - 30	Metal extraction and separation from concentrated wastes
2	10^{-2} - 10^{-6}	1000-20000	4 - 20	65 - 10	Metal extraction, separation, electrosynthesis
3	10^{-2} - 10^{-7}	1000 - 10000	4 - 50	55 - 20	Extraction of organic compounds, electrosynthesis
4	10^{-4}-10^{-8}	1000 - 10000	4 - 50	80 - 30	Extraction of ions from very dilute solutions

SUMMARY

The technologies described could be used for:

(i) Electrowinning of non-ferrous metals from technological electrolytes and rinse waters in beds of non-conductive (glass) particles;

(ii) Separation of non-ferrous metals and their refining in the fluidized bed electrode (FBE, metallic particles);

(iii) Electrosorption of organic contaminants from dilute solutions, including drinking water using granulated carbon materials;

(iv) Selective removal of non-ferrous metal ions from dilute technological wastes on inorganic IEMs with electrochemical regeneration of the exchangers;
(v) Electrodeposition of metals from dilute solutions using a dynamic bed of inorganic ion-exchange materials.

The technologies and the pilot and industrial reactors developed are employed for the following processes:
(i) Highly efficient extraction from electrolytes of nickel, free from electropositive metals and direct purification of nickel from partially reduced nickel oxide (FBE);
(ii) Metal removal from effluents of electroplating plants (FBE);
(iii) Electrochemical synthesis of organic compounds and treatment of biological fluids (FBE from carbon-containing materials).
At present, more than 180 different reactors are employed in hydrometallurgical and electroplating processes.

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COLD PLASMA AS A NEW TOOL FOR PURIFICATION OF WASTEWATER

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INTRODUCTION

Currently, scientists and experts from many countries are working on the development and implementation of new technologies for drinking water and wastewater purification based on various physical and chemical methods. These technologies are intended to resolve some important environmental and resource conservation problems, such as purification of industrial sewage from galvanic, electrochemical and other hazardous chemical processes, purification of municipal and household sewage, purification of sewage from organic compound productions and oil-refineries, purification of microbiological and radioactive sewage, activation of chemically pure water and many others. In addition, the problem of high purification of sewage from heavy metals, inorganic and organic admixtures, including diluted solutions, has not been solved yet. The solution of the above-mentioned problems will help citizens to adapt to the modern complex ecological conditions and increase their living standards.

During the last ten years, significant progress has been achieved in the development of new methods of water treatment based on electrochemical and plasma-chemical principles. On the basis of these scientific achievements, several pilot plants and other industrial units were built and successfully deployed.

The most promising are the methods based on the application of non-equilibrium low-temperature glow discharge plasma (GDP) (Hickling and Engran 1964). They have a number of advantages, such as (i) smaller dimensions of the equipment, (ii) opportunity to automate both the process and the quality control of processed media, (iii) low requirement for human resources, (iv) opportunity to use new solutions. Although the properties of

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these new methods are poorly investigated, they have demonstrated potentially useful features. The basis for the process is the contact plasma discharge on the surface of a liquid phase formed between an electrode in a gas phase and the surface of a liquid, into which the second electrode is immersed. GDP acts as a source of chemically active atoms and molecules in a liquid causing a number of chemical reactions of redox character (Takasaki and Harada 1986).

The important characteristics of non-equilibrium, low-temperature contact plasma are as follows: (i) the power required for the discharge generation and maintenance, which decreases upon reducing pressure, (ii) the liquid layer thickness, and (iii) the conductivity of the liquid.

CHEMICAL PROCESSES IN WATER INDUCED BY NON-EQUILIBRIUM LOW-TEMPERATURE PLASMA

The primary actions of non-equilibrium contact plasma are the generation of ions, excited water molecules and secondary electrons:

$$H_2O + e^- \rightarrow H_2O^+ + 2\,e^-$$
$$H_2O + e^- \rightarrow H_2O^* + e^-$$

Once created, the particles disappear in accordance with the reactions below:

$$H_2O + H_2O^+ \rightarrow H_3O^+ + OH^{\cdot}$$
$$e^- + H_2O \rightarrow e^-_s + H_2O$$
$$H_2O^* + H_2O^* \rightarrow H_2O_2 + 2H^{\cdot}$$
$$H_2O^* \rightarrow OH^{\cdot} + H^{\cdot}$$

where e^-_s is the hydrated electron.

It is known that, during this event, several ion pairs are formed around six excited water molecules, which can produce up to nine radical pairs. Consequently, the initial concentration of such particles in the solution is rather high; therefore, the rate of recombination of radicals (Eqs. 1-4), causing formation of the activation products, is greatly increased.

$$OH^{\cdot} + H^{\cdot} \rightarrow H_2O \qquad (1)$$
$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \qquad (2)$$
$$H^{\cdot} + H^{\cdot} \rightarrow H_2 \qquad (3)$$
$$e^-_s + e^-_s + 2H_2O \rightarrow H_2 + 2OH^- \qquad (4)$$

If an electric field is applied to the solution, the motion of the ions is mainly chaotic, however, one of the directions becomes predominant. The rate of movement of ions in the electric field increases upon increasing the gradient of the electric potential.

If the active particles are distributed homogeneously enough, they play an essential role in radical-molecular reactions, for example

$$H_2 + OH^{\cdot} \rightarrow H_2O + H^{\cdot}$$
$$H_2O_2 + H^{\cdot} \rightarrow H_2O + OH^{\cdot}$$
$$H_2O_2 + e^-_s \rightarrow OH^{\cdot} + OH^-$$
$$H_2O_2 + H_2O^* \rightarrow H_2O + 2OH^{\cdot}$$

These reactions lead to the chain mechanism of water decomposition and generation of peroxide and superoxide compounds. Besides the above particles, insignificant quantities of hydrogen peroxide radicals $HO_2^{\cdot}$ are formed in water under the action of non-equilibrium contact plasma:

$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + HO_2^{\cdot}$$

In water containing dissolved oxygen, the process of the radical formation is especially intensive:

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}$$
$$H^+ + e^-_s + O_2 \rightarrow HO_2^{\cdot}$$

In turn, the hydrogen peroxide radical can promote generation of oxygen according to the reactions below:

$$H_2O + OH^{\cdot} \rightarrow H_2 + HO_2^{\cdot}$$
$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$$
$$H_2O_2 + HO_2^{\cdot} \rightarrow O_2 + H_2O + OH^{\cdot}$$

The contact action of non-equilibrium plasma causes the formation of short-lived superoxide compounds, which additionally contributes to the structural water transformations and accumulation of hydrogen peroxide in it (see Fig. 1):

$$HO_2^{\cdot} + HO^{\cdot} \rightarrow H_2O_3$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_4$$

The $OH^{\cdot}$ radicals possess oxidative properties. Hydrogen peroxide may act as an oxidant or reducer depending on pH. Hydrated electrons and hydrogen peroxide in alkaline solution determines reducing properties, whereas in acid solutions this role is given to hydrogen atoms. In the presence of dissolved oxygen, hydrogen atoms and hydrated electrons are transformed into $HO_2^{\cdot}$ radicals (Pivovarov and Sergejeva 1999).

The products formed as a result of non-equilibrium contact plasma treatment determine the system reactivity. Under the availability of two (gaseous and liquid) phases, where electric current is transferred between the electrode submerged into the liquid and the electrode in the gaseous phase, the interface in which the intensive physico-chemical transformations occur because of its complex structure is of particular importance. There are several dynamic layers above the surface of the liquid, with various electrical charges therein. Positive electric potential forms a cloud of predominantly positive charges in the gas phase. The mechanism of ion movement inside the solvent consists of two stages. The first stage, which is attributed to all the ions, includes electric migration, i.e., ion displacement relative to the solvent mass due to the external electric field applied to the ions.

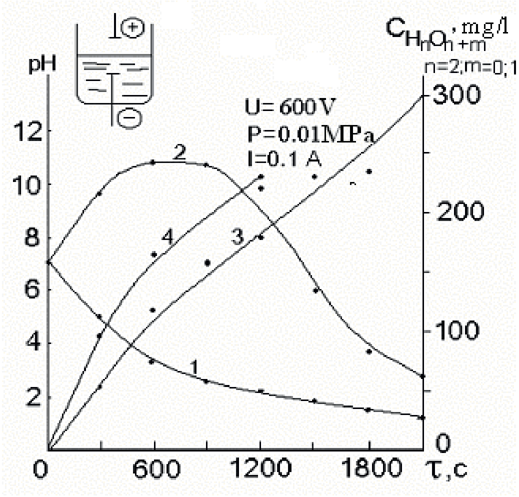
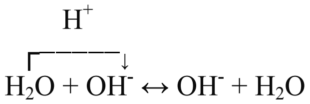


Figure1. Changes in pH (1, 2) and accumulation of H_2O_2 (3, 4) in water vs. time of treatment by low-temperature, contact plasma. 1, 3 – tap water; 2, 4-distilled water.

This stage promotes the ion mobility; however, its contribution to the overall ion transfer is insignificant. The other stage involves the directional chemical reaction of transferring protons between the adjacent particles of the solvent:

$$\overset{\overset{H^+}{\ulcorner\!\!-\!\!-\!\!-\!\!-\!\!\downarrow}}{H_3O^+ + H_2O} \leftrightarrow H_2O + H_3O^+ \qquad (5)$$



$$\overset{H^+}{H_2O + OH^- \leftrightarrow OH^- + H_2O}$$

These stages, in aggregate, lead to spatial transfer of the charge by the token mechanism. The peculiarity of the proton, as a charge carrier, is due to its mass and size, which are small enough to reveal its wave properties (e.g., tunnel effect) during its movement in the elementary event (reaction 5). This effect causes reduction of activation energy for elementary proton transfer and, subsequently, increases ion conductivity.

In the near-surface charge of the water, transfer of current in the liquid is provided by the products of auto-protolysis, namely, H_3O^+ and OH^-. Therein, H_3O^+ move toward the cathode and OH^- go to the interface. Ions H_3O^+ form H^+ and H_2 on the cathode acquiring one or two electrons from it. H_2 molecules coalesce into gas bubbles floating upward to the surface of the liquid, and hydrogen goes into the space above the liquid. The thickness of the near-surface layer of positive particles cannot exceed their path length. The layer is characterized by its flexible, which is changing in the process of liquid treatment. The drop of electric potential takes place at the gas-liquid interface; it is being flexible and changeable during the glow discharge contact action as well. Variations in the value of the near-surface potential are manifest in the initial accumulation of charges within a specific transfer time and their subsequent consumption. Changes in physical and chemical properties of water in the process of treatment are, first of all, determined by transformations in the near-surface layers of the liquid, ensuring transfer of current from the liquid to the gaseous phase.

The products formed, as a result of non-equilibrium contact plasma action, are utilized for interaction with the agents contained in the treated liquid medium. Firstly, it relates to solutions containing compounds of polyvalent metal ions, which are capable of changing their valence under the influence of active components in the treated solution.

The data on extraction of manganese compounds from various solutions can serve as an example of reduction process under the plasma action. During the treatment of moderately concentrated solutions having initial manganese content of $(1.7\text{-}3.5)\times10^{-4}$ M by GDP, the solution discoloration accompanied by simultaneous formation of a dark-brown precipitate of $MnO_2{\cdot}2H_2O$ is observed. The mechanism of manganese oxidation occurs according to the following scheme:

$$Mn(VII) \rightarrow Mn(IV)\downarrow \rightarrow Mn(II)$$

The degree of extraction of manganese compounds from such solutions reaches 95-98%.

As another example, the process of Fe^{2+} oxidation into Fe^{3+}, which could take place in solutions and wastewater, is presented below. It occurs according to the reactions:

$$
\begin{aligned}
&Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^{-}\\
&Fe^{2+} + HO^{\cdot}_{2} \rightarrow Fe^{3+} + HO_2^{-}\\
&HO_2^{-} + H^{+} \rightarrow H_2O_2\\
&2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+}\downarrow + 2OH^{-}\\
&2Fe^{2+} + H_2O_2 + 2H^{+} \rightarrow 2Fe^{3+}\downarrow + 2H_2O
\end{aligned}
$$

The iron hydroxide formed could easily be isolated using well-known methods of inhomogeneous liquid systems separation.

The non-equilibrium, low-temperature contact plasma inducing the formation of highly reactive particles in liquid media could be used for efficient disinfection of water and wastewater.

The size of bacterial cells range from 0.5-5.0 µm and they can be cylindrical, spherical or curled in shape. The average mass of bacterial cell is 4×10^{-12} g (Zadorognaya et al. 1993). The cell is covered with a shell 10-40 nm thick, which is durable and stable to external factors. This shell is composed of proteins, mucopolysaccharides, mucoproteins, lipids, and sugar. The important feature of many bacteria is swelling of their membranes with formation of a mucous layer (capsule). This layer reaches a thickness comparable with the cell size (~ 0.2 µm) and looks like a high-viscosity gel, which includes glucose, sucrose, fructose, gluconic acids, gelatin, and other substances. The capsules present a perfect shield to the destructive action of antibodies in a number of pathogenic bacteria. Sometimes, the mucus encloses several hundred cells forming so-called zooglea, i.e., a jelly-like matrix. In addition, on the surface of various cells there are some appendices, e.g., flagella, fimbria, etc. These consist of proteins and provide some kind of "reinforcement" to the mucous layers, generating a specific hydrophilic system. Under the cell shell, there is a cytoplasmic membrane, 5-10 nm thick, which consists of lipoprotein and ribonucleic acid complexes. The membrane acts as an osmotic barrier concentrating nutrients inside the cell and promoting secretion of metabolic products outside. The cytoplasmic membrane encloses a cytoplasm, i.e., a complex of colloidal substances and cell organelles, the viscosity of which is 10^{3}-10^{4} times higher than that of water. The cytoplasm of each cell contains up to 10^{4} ribosomes, 20-40 nm in size, consisting of proteins, phospholipids and RNA. There is no strongly pronounced nucleus in most cases. In superfine sections, only the nuclear vacuole is observed, with a bunch of DNA filaments.

The mechanism of microorganism inactivation is not completely understood at present. Some researchers suppose that the blockage of cytoplasmic membranes by certain chemical agents is enough for inactivation of bacteria. The possibility of interaction of the agents with membrane components is not ruled out either. Other researchers suggest that disinfecting reagents should penetrate into a cell to exert their action. Dysbolism is considered as the secondary cause of disinfection. It was suggested that DNA is the main target for all antimicrobial agents, since they cause irreversible changes to it. This means that antimicrobial agents should directly attack DNA. Therefore, it is evident that the rate of disinfection is determined by the rate of disinfecting agent penetration into the cell and the speed of cell death as a result of metabolism failure. The bactericide effect is mainly due to formation of oxidants, e.g., free radicals and their derivatives. The treatment of aqueous media containing microorganisms by non-equilibrium, low-temperature contact plasma, destroys purine and pyramidine rings in bacterial cells. Enzymes, which contain free sulfhydryl groups or require fermentation process for them, are the most sensitive to plasma-chemical inactivation. Water treated by GDP demonstrates a number of special features, such as accumulation of hydrogen peroxide and super-peroxide compounds, and retention of compounds with increased oxidising abilities as well as a stable cluster structure (Prilutsky and Bahir 1997).

The experiments performed in our laboratory verified the presence of active oxygen-containing particles in the treated water. In these experiments, the cathode, made of platinum, submerged into the water was subjected to GDP, and, after a certain period of time, catalytic reaction of hydrogen formation and release of oxygen-containing compounds was observed. The reaction was accompanied by the appearance of light flashes in aqueous medium. The mobility and number of charged particles in treated water has been experimentally established.

EXPERIMENTAL RESULTS

The experiments presented below have been conducted using a unit consisting of a batch reactor, power module, vacuum pump, and controllers (Fig. 2). Working parameters of the unit were as following:

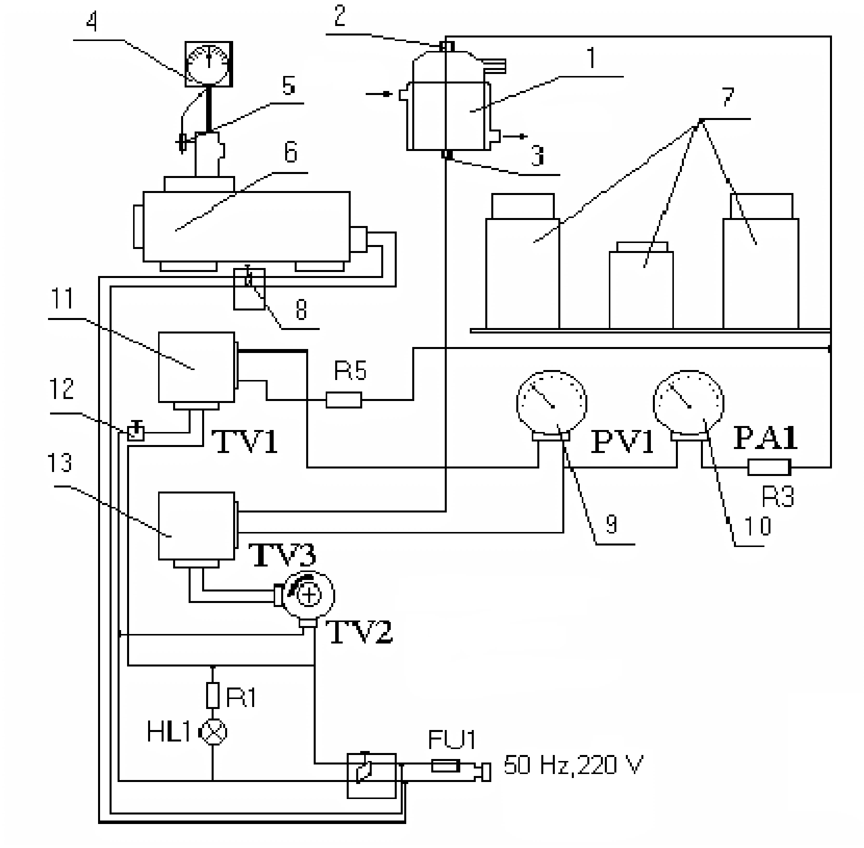


Figure 2. 1- reactor, 2 – anode, 3 – cathode, 4 - vacuum-meter, 5 – pressure-sensitive switch, 6 - vacuum pump, 7 - water separators, 8 - oil filter, 9 – ammeter PA1, 10 – voltmeter PV1, 11 and 13 - power sources, 12 – regulator of voltage. TV1, TV2, TV3 - current transformers; FU1-fuse; HL1- signaling bulb.

current I = 15-150 mA, voltage U = 450-1000 V, temperature in the reaction zone T = 283-320 K, pressure $P = 1\times10^4$ Pa, the distance between anode and surface of the liquid was h = 5-15 mm, and the volume of liquid V = 40 mL.

Example 1. The 1.6 mm-thick film of wastewater containing 22 mg/L Fe^{2+}, 55.5 mg/L Cr^{6+}, 14.3 mg/L Ni^{2+}, 8 mg/L Mo^{4+}, and 6 mg/L Co^{2+} at pH 7 was treated by GDP. The pressure in the reactor was 5×10^4 Pa and the temperature of the liquid at the reactor inlet was T=293 K. As a result of treatment, the concentration of metal ions was reduced down to the level of maximum permissible concentration (MPC).

Example 2. Wastewater containing 150 mg/L Zn^{2+}, 5.02 mg/L Cd^{2+}, 2 mg/L Cu^{2+} at pH 10 was passed through the plasma discharge reaction zone.

The thickness of the liquid layer was 1.6 mm and temperature of the liquid at the reactor inlet was T = 293 K. This treatment resulted in reduction of Zn^{2+} concentration to 0.05 mg/L and Cd^{2+} to 2 mg/L. Cu^{2+} was not found in wastewater after treatment.

Example 3. Water solution containing 0.1 % CN^- was treated by GDP featuring the following parameters: current 100 mA, voltage 600, liquid layer 1.6 mm thick, pressure in the reactor 5×10^4 Pa, distance from the liquid surface to the electrode in gaseous phase 10 mm, and temperature of the liquid at the reactor inlet 293 K. The samples were 100 % purified.

Example 4. The study into inactivation of coliphages in wastewater was carried out with the use of synthetic and filtered natural wastewater. The data obtained demonstrated that, after 1 min of treatment by GDP, the wastewater coliphages were inactivated by about 70 % in synthetic wastewater and by about 98 % in the filtrates, respectively. After 3 min of treatment by GDP, the degree of inactivation practically attained 100 % in both cases.

Example 5. We have studied the disinfection of drinking water containing ~1-100 PFU/L, which is the most common level of coliphage content after conventional water purification, using GDP. The results show that, in drinking water containing ~100 PFU/L, the degree of inactivation attained about 50 % and 100 % after 1-min and 3-min treatments, respectively. At a lower level of contamination (~10 PFU/L), 1-min treatment was usually enough for complete inactivation of coliphages. The time necessary for complete inactivation of coliphages, depended on their initial concentration in water. However, the data obtained showed that a 3-min long GDP treatment maximized the decrease of the coliphage content in drinking water (essentially to a completion of disinfection) irrespective of the initial contamination.

Example 6. Along with the above research, the GDP effect on the inactivation of polioviruses was studied. The polioviruses contained in drinking water at a level of 10^3 of virions per 1 mL, were inactivated by ~45 % and by 99.9 % after 1-min and 3-min GDP treatments, respectively. Complete inactivation of the viruses was observed after a 5-min GDP treatment. At an initial content level of the viruses in drinking water of 100 PFU/mL, they were not detected after a 3-min GDP treatment. At the lowest concentration of the viruses in drinking water (when only a few virions per mL were present), they were not detected in water after just a 1-min GDP treatment.

Although the method of GDP treatment described above allowed cost efficient separation and removal of naturally occurring contaminants, this technology, in general, has not been applied beyond laboratory studies and the experimental data is still quite limited. Systematic physico-chemical and technological studies of this new method is much needed for its further development. Nevertheless, recent technological advances made by Ukrainian scientists offer an attractive opportunity for implementation of this method into industrial practice.

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PURIFICATION OF INDUSTRIAL WATERS FROM ORGANIC COMPOUNDS AND BACTERIA

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INTRODUCTION

At present, numerous anthropogenic substances are found in the biosphere. A number of international organizations recognize the great danger of dioxins, polychlorobiphenyls and chlorine- and phosphorus-containing pesticides from the point of view of toxicology, hygiene and ecology. About 70 % of them are accumulated in soil, 15-20 % - in open and closed water reservoirs, and the rest - in flora and fauna. Pesticides represent a special danger because they are being stored in Ukraine, as well as in some other countries, in enormous amounts exceeding tens of thousands of tons. They are stored in inappropriate containers for a long time. The release of the pesticides into the environment can lead to dangerous social and economic consequences for the countries. Therefore, in this work we analyze the toxicity of water polluted with pesticides with respect to plants, water organisms and bacteria. The necessity for effective destruction of pesticides residing in the environment is obvious. We suggest that such a powerful technology as plasma treatment is appropriate for this purpose (Malik et al. 2001, Blaisot et al. 2001).

The development of modern medical science is impossible without improvement of the methods of water disinfection from active microorganisms. A number of methods for deactivation of bacteria are known. For example, the disinfection could be conducted by the application of high pressure and temperature or with the help of various chemicals. However, these methods are not suitable in some cases. The use of chemicals for this purpose requires their eventual neutralization and utilization since those chemicals could be hazardous to human health. Therefore, the

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development of essentially new technologies for sterilization of water is necessary.

The radiation treatment of water is one effective method for its purification from microorganisms without chemicals. The efficiency of this method stems from the interaction of microorganisms with active particles, e.g., oxidizers of organic molecules, which are produced as a result of water radiolysis. The use of chemicals is not required. However, radiation treatment is expensive and hazardous, and the relevant equipment is very complex.

Physical methods of water treatment based on electrical discharges also allow the formation of chemically active particles directly in the gas or liquid phases. The method of water purification from bacteria using low-temperature and low-pressure plasmas formed by electric discharges was developed in our laboratory. This method operates just as well as radiolysis. The results of water sterilization in a plasmo-chemical reactor based on barrier gas discharge have been presented in (Chernyak et al. 2001). The possibility of water sterilization by a new method based on secondary discharge with a “liquid” electrode is also discussed in this work.

MATERIALS AND METHODS

The method of plasma destruction of organic molecules and micelles in water was studied using cationic (tetradecylpyridinium bromide and cetyltrimethylammonium bromide) and anionic (sodium dodecylsulfate) surfactants. The concentration of surfactants in water ranged from 10^{-3} to 10^{-1} M. To study the possibility of surfactant destruction in colloidal systems, oil-water emulsions were prepared with 4 g/L of oil. The emulsions were stabilized by 10^{-3} M anionic surfactants.

As an object of the research, we also used the toxic agent 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl) ethane (DDT), chemical formula $(C_6H_4Cl)_2CHCCl_3$, as an example of a chlorine-containing pesticide (highly dispersed clay/surfactant/DDT: 0.65/0.05/0.30 by weight). It is emulsified in water because of presence of surfactants. The prepared water emulsion contained 1g/L DDT.

The treatment of aqueous media containing DDT and surfactants was carried out in the plasmo-chemical reactor (Fig. 1). The detailed description of the reactor is presented elsewhere (Chernyak et al. 2002a, b). The reactor consists of a glass cylinder (1) with a cover (3). The arc discharge of an alternating current I_s occurs between graphite electrodes (4) in a gaseous phase. It forms a stream of charged particles and radicals (7). They move into the liquid to be processed with the help of a stream (5) of air or water vapor. The gas release valve (6) is built into the cover of the reactor. The chemical reactions take place in a small diffusion layer (8) of the solution. Solution mixing takes place as a result of convection flows. A constant voltage was applied to the auxiliary electrode (2) immersed in the liquid. The polarity of this electrode and the value of current I_d could be altered to study the efficiency of destruction of organic molecules under various conditions. The system works at atmospheric pressure.

To evaluate the destruction of DDT and surfactants in aqueous media under the influence of the plasma discharge, the absorption spectra over the wavelength 200–600 nm was monitored. Preliminary investigations demonstrated that the absorption coefficient of solutions is a linear function of concentration over a wide range of concentrations. All the concentrated solutions of DDT were diluted by 20 times with water before spectrometry.

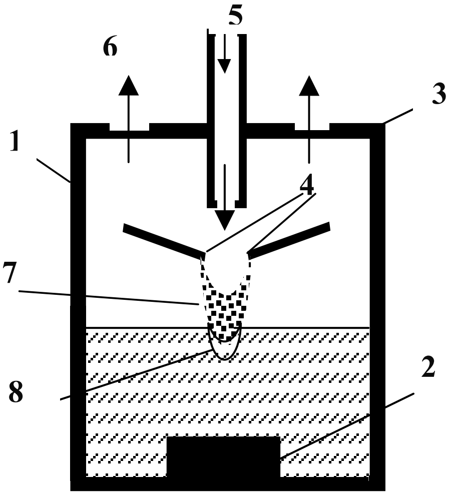

Figure 1. Plasmo-chemical reactor for water treatment in a stationary regime.

The evaluation of toxicity of the water and the products of destruction after the plasma treatment was conducted using *Daphnia magna* in accordance with standard techniques. The velocity and character of movement of the test organisms were monitored. The lethal dose, LD_{50}, i.e., the concentration of toxic substances required to kill 50 % of the exposed organisms was determined.

A culture of *Escherichia coli* in distilled water was used as the model system for evaluation of the plasma discharge effect on microorganisms. The sterilization effect was studied in several working regimes of the plasmo-chemical reactor. The amount of surviving bacteria was corrected with respect to the increase of colonies during the 24 hours after the plasma treatment. A culture incubated in distilled water without plasma treatment was used as a control.

RESULTS AND DISCUSSION

In general, the proposed plasmo-chemical reactor may be considered as a common electrochemical cell with “liquid” and plasma electrodes. At the same time, this system has more opportunities for regulation as compared to the electrochemical cell. For example, one can change the type of gas for plasma generation, the value of current, and polarity of the “liquid” electrodes. By doing so, plasma of various structures may be generated and this affects the way in which the plasma discharges react with organic substances present in aqueous media. In some cases, it caused oxidative destruction, in others - a regenerative effect was observed.

Studies of the destruction of pesticides and surfactants by plasma discharge were carried out at 300–600 mA for arc discharge (I_s), and from –450 mA (a condition of so-called "liquid" cathode) to +450 mA (a condition of the "liquid" anode) for secondary discharge (I_d). The time of treatment was varied from 1 to 6 min.

The absorption spectra of tetradecylpyridinium bromide in water before and after 3-min plasma treatment with a current I_d=150 mA and water vapour as a plasma-generating gas is presented in Fig. 2. A considerable decrease of absorption coefficient *k* at wavelength 265 nm confirming efficient surfactant destruction (up to 90%) was observed. In general, the absorption increased throughout entire wavelength range due to synthesis of active oxidizers directly in the water under the influence of the plasma discharge. It was shown previously (Chernyak et al. 2002a) that nitric acid, nitrous acid and hydrogen peroxide are synthesized. Importantly, the quantity and type of oxidizers depend on the working regime of the reactor and this can be regulated according to practical needs.

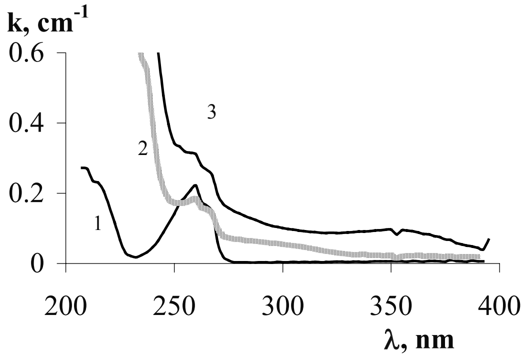

Figure 2. Absorption spectra of tetradecylpyridinium bromide (4.72 mg/L): 1 – solution before treatment, 2 – solution after treatment in regime with “liquid” cathode and 3 – solution after treatment in regime with “liquid” anode.

According to the absorption spectra of pesticide emulsions after the plasmo-chemical treatment, diminution of DDT (up to 70 %) was observed for some working regimes of the reactor. The results of treatment at some secondary discharge currents for 3 minutes are presented in Fig. 3. Water vapour was used as the plasma-creating gas in both regimes, i.e., with “liquid” anode (curves 2, 3) and “liquid” cathode (4, 5). Although the absorption peak at 324 nm is not sharp, linear dependence of *k* for the DDT concentration is observed in the range 10-100 ppm. It allows quite accurate estimation of the destruction rate. As a result of these experiments, the possibility to destroy DDT in aqueous media was confirmed. It was also concluded that the destruction rate depends on I_d. By using a special scheme of feeding the concentrated DDT solution into the active zone of the plasma reactor, DDT destruction was increased to 85%.

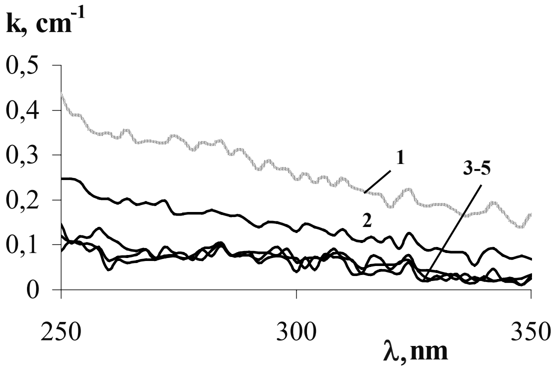

Figure 3. Absorption spectra of DDT before (1) and after plasma treatment at various I_d: +300 mA (2), +450 mA (3); –300 mA (4), –450 mA (5).

The extent of destruction of oil-water emulsions stabilized by anionic surfactants reached 60% after treatment for 3 min. Pure oil can be collected from the water surface after treatment of the emulsion using a “liquid” anode at I_d=200 mA and I_s=400 mA. This means that the plasma discharge destroys surfactants adsorbed on the surface of the oil drops. Oil-water emulsions have been transformed into suspensions under plasma treatment with a “liquid” cathode. The observed polymerization of oil serves as evidence of the large impact of the plasma stream on substances in aqueous medium. The destruction, in water, of the organic compounds studied increases with increasing current of the secondary discharge and with change of the regime of treatment from "liquid" anode to "liquid" cathode mode.

The efficiency of plasmo-chemical treatment depends also on the structure of the plasma torch. This is determined by the delivery rate of the plasma-generating gas and by the current of the arc discharge. These external independent parameters ensure the flexibility of the technological process and permit feedback for continuous control of the plasmo-chemical reactor. In such a multi-factor system, feedback is necessary to control the extent of destruction and the composition of output products. At present, the exact mechanism of chemical processes during plasmo-chemical destruction of organic substances in aqueous media is poorly understood. However, the minimization of toxicity of the output solutions could be targeted during optimisation of reactor parameters for achievement of effective water treatment.

The acute toxicity of the aqueous solutions of DDT after their plasmo-chemical treatment can be tested using *Daphnia magna.* The culture was handled according to ISO 6341-82. Few juvenile *Daphnia magna*, not older than 48 hours, were selected for each test run. They were placed in a 5 mL test sample. The time needed to kill all organisms was monitored. Distilled water was used as the control solution since the organisms do not perish in it for the length of observation. Morphological changes of living organisms and decrease of their vitality under the action of treated aqueous solutions were determined by visual inspection. Vitality was assessed by observation of the character of movement of the organisms.

Water emulsions containing 10 mg/L DDT were processed in the plasmo-chemical reactor at various values of I_d (50, 100, 150, and 200 mA) with positive and negative polarity of a “liquid” electrode and with water vapor as the plasma-creating gas.

The resulting biotesting using *Daphnia magna* show that the toxicity of the products of DDT destruction is smaller than that of the initial solution independent of the working regimes of the reactor. Plasmo-chemical treatment of water leads not only to destruction of organic molecules, but also to death of bacteria. Cultivation of *Escherichia coli* in water subjected to the barrier plasma discharge was studied in (Chernyak et al. 2001a). In the present study, we assessed the sterilization of the water treated with a secondary plasma discharge with a “liquid” electrode under the conditions described above. The secondary discharge current I_d varied from 0 to 100 mA, and the current of the arc discharge I_s - from 200 to 400 mA.

It was established that the degree of suppression of the vital ability of microorganisms depends on the working regime of the plasmo-chemical reactor. The degree of sterilization increases with increasing time of treatment and the currents of the arc and secondary discharges. Complete sterilization of the bacteria solutions was achieved after treatment for 1 min at I_d=100 mA and I_s=200 mA. The influence of plasma in the “liquid” cathode mode is stronger, as full sterilization of a solution is achieved within 40 s. This mode should be used for actual working devices for water disinfection. If a solution with bacteria was processed for 3 min using the regime with the bottom electrode switched off and administration of vapour to the area of the arc discharge, the bacteria also were totally killed and complete sterilization of water was achieved.

CONCLUSIONS

The application of non-equilibrium plasmo-chemical technology for the destruction of organic substances in water is described. The possibility of achieving considerable destruction of various organic substances accompanied by reduction of the total toxicity of solutions has been demonstrated. The extent of destruction reached 90 % for surfactants in water solutions and 70 % for an emulsion of DDT. The extent of destruction of oil-water emulsions stabilized with anionic surfactants was 60% after a 3-min treatment. In this case, pure oil can be collected from the water surface.

The general toxicity of pesticide emulsions containing DDT was slightly reduced after plasmo-chemical treatment. Since the destruction of the DDT was established by chemical analysis, the toxicity is possibly caused by active particles formed by radiolysis of water and destruction of pesticide molecules.

In combination with additional modern biochemical methods of purification of water after plasmo-chemical treatment, it is possible to create an effective system of industrial sewage decontamination from dangerous toxic pollutants. In this way the organic substances can be destroyed directly in the solution.

Plasmo-chemical treatment can also be used for decontamination of water from bacteria and viruses. The treatment leads to suppression of vital ability, breakdown of the cellular membranes, and, eventually, to death of the microorganisms.

The technology of plasmo-chemical destruction of organic molecules and sterilization of water can be applied to the design of novel water purification systems.

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PART IV

MANAGEMENT OF WATER RESOURCES, PLANNING, TRAINING AND EDUCATION IN WATER TREATMENT

INDUSTRY UNIVERSITY COOPERATION FOR POSTGRADUATE EDUCATION AND TRAINING IN THE WATER TREATMENT AREA

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INTRODUCTION

The longest established and most high profile mechanism for cooperation between industry and academe is the US National Science Foundation's Industry/University Cooperative Research Centre (I/UCRC) Programme. Over the past three decades, I/UCRCs have led the way to a new era of partnership between universities and industry, featuring high-quality, industrially relevant fundamental research, strong industrial support of and collaboration in research and education, and direct transfer of university developed ideas, research results, and technology to U.S. industry to improve its competitive position in world markets. Through innovative education of talented graduate and undergraduate students, the I/UCRCs are providing the next generation of scientists and engineers with a broad, industrially oriented perspective on science and engineering research and practice.

Currently there are more than 50 I/UCRCs, with more than 750 faculty members, some 750 graduate students and 200 undergraduate students who carry out the research at these Centres. Almost the entire spectrum of current technological fields is encompassed. A primary purpose of the I/UCRC Programme is providing high-quality interdisciplinary education. The Centres have produced several thousand M.S. and Ph.D. graduates, who can be found throughout American industry and academe.

This mechanism is robust, effective and suitable for transfer to other countries. It is also very suitable for the water treatment area.

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HOW DOES IT WORK?

An I/UCRC usually begins with a small planning grant to a university professor who seems to exhibit the scientific, organizational, and entrepreneurial skills necessary to form a team and initiate and run a successful Centre (Gray et al. 1998). If the prospective Centre can obtain commitments of strong support from industry and the affiliated university or universities, it may submit a proposal to NSF describing the progress that has been made and documenting the team's potential to operate successfully as an I/UCRC. Two or more universities may also jointly propose a multi-university Centre. Following a successful review of the proposal, NSF may make an initial five-year I/UCRC award of $70,000 annually to the Centre team. When the initial five-year grant expires, NSF funding may be extended at a reduced level of $35,000 annually for an additional five years. In its final year of I/UCRC Programme support, a Centre may compete for a new I/UCRC award based on a proposed research and education programme involving significantly new intellectual substance.

NSF's investment in the I/UCRCs is intended to seed partnered approaches to new or emerging research areas, not to sustain the Centres indefinitely. The Foundation intends for I/UCRCs gradually to become fully supported by university, industry, state, and/or other non-NSF sponsors. Each I/UCRC is expected to maintain at least $300,000 of industrial support through Membership fees, at least six industrial Members, and a plan to work toward self-sufficiency from NSF.

In addition to the basic I/UCRC award, Centres and Centre researchers can compete for other NSF support for research and education projects. At any point - even at the end of its life cycle - NSF may provide funding to the Centre under special arrangements involving joint participation by other NSF Programme offices. NSF supplemental support may include collateral programmes such as a TIE project, whereby two or more Centres and their industrial Members engage in a cooperative research project of interest to all parties (with NSF and industry sharing costs). Through Programmes such as GOALI (Grant Opportunities for Academic Liaison with Industry), fellowships are offered to Centre faculty, whereby the faculty member can spend time in a corporate research lab or factory, again with NSF sharing the cost. Other supplements to I/UCRC awards may be made in the form of joint sponsorship of projects with other federal agencies, Research Experiences for Undergraduates and other educational activities, workshops, and other purposes consistent with the goals of the Programme.

THE STRUCTURE OF A TYPICAL I/UCRC

The Centre Director reports to university management - in most cases, directly to the Dean of Engineering. An Academic Policy Committee composed of the deans of engineering and science and other top university officials such as the provost and vice president for research is available to address important policy issues such as patents and licensing, promotion, and tenure. The various research Programmes usually consist of several projects with a coherent focus on an industrial interest; they are pursued by graduate students under the direction of faculty researchers.

Across the Programme, these centres have established an extraordinarily effective partnership with industry. This partnership takes full advantage of the strength of each participant. University faculty contribute their skills in research and their understanding of the knowledge base; industrial researchers contribute their knowledge of both the technical needs of industry and the challenges associated with competing successfully in the marketplace. The partnership is formalized in each Centre's Industrial Advisory Board (IAB), which advises the Centre's management on all aspects of the Centre, from research project selection and evaluation to strategic planning. It is important to note that all IAB Members have common ownership of the entire I/UCRC research portfolio; however, individual firms can provide additional support for specific "enhancement" projects.

The partnership is given even greater depth through the direct involvement of industry representatives in research projects. Each project in the Centre has a principal researcher (typically the project's research professor) and in many cases also has a monitor from industry (who may be an IAB representative or an engineer assigned from an IAB member company). The principal researcher maintains close oversight of the progress of the research by the student(s) and briefs the industrial monitor on a regular basis. The monitor can, and often does, have direct input into the direction of the research.

This extensive industrial involvement in research planning and review leads to direct technology transfer, bridging the gap that traditionally has kept U.S. industry from capitalizing fully and quickly on the fruits of research at American universities. The close involvement of industry in the Centres also eliminates the perennial problem of "Not Invented Here"; in the cooperative research model, all Centre developed research products are owned by all the Members.

The participation of NSF, although small financially, nevertheless sets the tone for the I/UCRCs. Strong Programme management ensures that each of the centres continues to follow the I/UCRC model - each in its individual fashion - and that each remains strong. With such extensive industrial support and participation, NSF's role is crucial in influencing industry to take a longer-term view of its needs, with appropriate attention to research quality. This ensures that the fundamental research conducted in the Centres continues to add to the knowledge base that will be vital for solving the problems and meeting the needs of the future.

NSF also helps to ensure high standards among the I/UCRCs through a mechanism that is unique to this Programme: Independent professional Evaluators are engaged to study the industry university interaction on site, both qualitatively and quantitatively, to determine (1) the quality and impact of Centre research, (2) the satisfaction level of faculty who participate in the Programme, and (3) the degree of satisfaction of industrial participants. A historical profile of each Centre is maintained; and annual assessments are conducted of Centre processes and results, finances, and structural issues. One indication of the high quality of I/UCRC research is that faculty publish their work in the most prestigious journals. I/UCRC faculty as well as students regularly win awards from the professional societies for their innovative research.

INDICATORS OF SUCCESS

Perhaps the strongest indication of the value of these Centres to industry is the continued and growing participation of industry, even during periods of economic fluctuation. While industrial in house R&D continues to decline nationally, another indicator of the positive impact the I/UCRCs are having is the R&D activity they spark among their Members. In FY 2000, I/UCRC research resulted in at least $75 million in "follow on" R&D funding investments by member firms. The total industrial R&D investment attributable to the I/UCRCs in FY 2000 came to almost $100 million. This "new money" investment by I/UCRC Members may be the most tangible evidence that successful transfer of knowledge and ideas is occurring. The follow-on investment by companies demonstrates that they derive something from the I/UCRCs that they believe merits further development and commercialisation.

Not only have its members recognized the Programme’s long record of success in this arena. In 1998, the Technology Transfer Society of America, a national organization of public and private sector technology transfer professionals, bestowed on the I/UCRC Programme its Justin Morrill award. This award is given annually to an organization that has an "exemplary record of transfer of technology and also has made outstanding contributions to the theory and practices of technology transfer that are widely used by others." A further indication of the efficacy of the model is its successful transfer to Northern Ireland, described later.

TYPICAL I/UCRC MEMBER PRIVILEGES

(i) No overhead rate applied to Membership fees.
(ii) Opportunities to work closely with Centre students.
(iii) Non-exclusive royalty-free rights for in-house use of inventions and software developed by the Centre.
(iv) Voting Membership on the Industrial Advisory Board.
(v) Opportunity to serve as a mentor on any number of Technical Advisory Committees of the Centre.
(vi) Priority enrolment at reduced cost in short courses, workshops and conferences organized by the Centre.
(vii) Priority access to R&D facilities and other instrumentation in the Centre at a nominal fee to cover operation costs.
(viii) Free copies of all IUCRC reports & publications.

TRANSFER OF THE CONCEPT TO NORTHERN IRELAND

In 1986, the author explored the concept at the NSF in Washington, DC and five operating centres across the USA. This fact-finding tour suggested strongly that the concept was robust and eminently suitable for transplantation to the UK. Thus, armed with Centre Planning Manuals generously provided by Dr Alex Schwarzkopf, the Program Director, planning started to build a Centre in The Queen's University of Belfast. With a small industry base it was decided to focus on an area that would have relevance to as wide a cross section of industry as possible and have as much expertise within Queen's as possible. With this in mind, environmental science and technology was chosen and this lead to the name of the Centre, QUESTOR, (Queen's University Environmental Science and TechnOlogy Research).

Obviously the NSF could not provide a planning grant to a university in another country so a source of funds was needed. It was fortunate that the International Fund for Ireland (IFI) was being set up at the same time and a planning Grant of $107,000 was secured. This allowed the author to spend time visiting industry and trying to sell the concept. With no track record for the concept in the UK this was a very difficult task. (It should be noted here that with the ongoing successes of the QUESTOR Centre and its subsequent sister Centre called QUILL, also in Belfast, the transferability of the concept to another jurisdiction has been proven). In 1988, 27 companies were persuaded to attend a planning meeting in Belfast to discuss the possibility of setting up a Centre. At the end of this two-day meeting, nine companies indicated that they were willing to explore Membership further. There followed a busy period planning the research agenda to suit the nine companies as closely as possible and secure follow-on funding of $1,122,000 from the IFI for the first five years of the Centre. In May 1989, the Centre was founded with nine Founder Members.

The QUESTOR Centre is still running today and it is self-funding with Membership fees from industry and various Government funding agencies. In total the funding secured by the Centre during the thirteen-year period to 2002 was in excess of $38 million. This level of funding results in a leverage ratio of over six, and an individual Member leverage ratio of over 100. In other words, for every dollar contributed as membership fees by a Member they get access to over 100 dollars worth of generic research.

Arising directly from work being carried out in the Centre and at the suggestion of interested Members a second Centre was set up in Queen's to use the concept for ionic liquid research. This Centre, called QUILL, has also been very successful and it has Members drawn from eight countries on four continents and postgraduates and research staff from fourteen countries on five continents. The wide-ranging Membership clearly demonstrates two different types of I/UCRC. The QUESTOR Centre with a broad focus and an industry Membership drawn mainly from the UK and Ireland and the QUILL Centre with a highly focussed research theme, world-leading expertise and a Membership drawn from across the globe.

LOCAL MODIFICATIONS TO THE NSF CONCEPT

In order to benefit from the extensive experience gained by the NSF, the QUESTOR Centre was modeled as closely as possible on the carefully prescribed I/UCRC model. However it was felt that to suit the local environment some changes were essential. The main change was the addition of a Centre Research Committee with a Membership consisting of every academic with a project funded by the Centre. This committee elects a chair every two years and he/she liases with the Centre Director. In this way involved academics have a direct voice in the running of the Centre.

A second modification is in the reporting structure for the Centre; in Queen's where the Centre has academic supervisors from both the Faculty of Science and the Faculty of Engineering the Centre Director reports to a Centre Policy Committee consisting of the Pro-Vice-Chancellor for Research, the Director of the University Research Office and the University's Director of Finance. This is very important as it allows the Centre to operate without getting involved in "turf wars" between the Faculties.

A third modification is the regular employment of postdoctoral fellows alongside the postgraduate students and elimination of undergraduate students from the research projects. This seems to suit the local conditions better and still provides a corpus of highly trained scientists and engineers for the Members and local industry.

LOCAL EXTENSIONS TO THE CONCEPT

It became evident after a number of years that there was a great need in Northern Ireland industry, particularly SMEs, for independent advice, testing and research consultancy. The QUESTOR postdoctoral fellows were eminently qualified to provide this as a result of their interactions with industry Members on highly relevant research projects. Yet they could not be diverted from their projects that were funded by the QUESTOR Members. Funding was then sought from the EU through the local Industrial Research and Technology Unit to set up a technology transfer arm called the QUESTOR Applied Technology Unit (ATU). This unit employed many of the postdoctoral fellows ending their project with QUESTOR and also postgraduates finishing their degree. There was immediately a great deal of synergy between QUESTOR and the ATU with the ATU often transferring technology from QUESTOR research projects to both Members and local non-Members. The ATU was also able to identify problems that needed research and these could be fed into the QUESTOR project identification process.

Another very important feature of the ATU was the development of training courses for industry using QUESTOR facilities and equipment and the expertise of academics working with QUESTOR. A variety of courses have been offered such as:

(i) Practical Waste Minimisation;
(ii) Operation and Control of Water and Effluent Treatment Plant;
(iii) Data Collection for Environmental Management;
(iv) Site Investigation Techniques for Contaminated Land;
(v) Environmental Communication.

Feedback from attendees has been very positive with one attendee commenting “If I had attended this course before I ordered my treatment plant I would have gone in a very different direction and saved a great deal of money”

A further more recent spin-off from QUESTOR via the ATU was the formation of QUESTOR Technologies Ltd., a stand-alone company that acts to commercialise research arising from QUESTOR. This company has three products in development, all related to water treatment:

(i) Sludgeguard – a test for *Microthrix parvicella;*
(ii) Biocol – a process for the removal of colour from textile effluent;
(iii) Biosettler – a process for improving the settling of activated sludge.

The existence of the company fits neatly into the overall scheme and it also feeds ideas into the Centre and draws upon the expertise created in the Centre.

FOCUS

The original Members defined the research focus of QUESTOR and as a result of this it was heavily focused on end-of-pipe solutions to industry problems. As a further consequence much of the research related to various aspects of water treatment and this theme has continued to this day. Some current projects are:
(i) Metal organic frameworks for treatment of wastewater;
(ii) Sludge minimization - investigation of a novel approach;
(iii) Use of seaweeds to remove heavy metals from wastewaters;
(iv) Improved removal of heavy metal contaminants from wastewater using chelating polyelectrolytes;
(v) Characterisation of *Microthrix parvicella* ;
(vi) Growth and its Relationship to the Incidence of Foam and Scum Formation in Activated Sludge;
(vii) The production of wastewater sludge for phosphate recovery

As the years passed the focus was expanded to include clean technology as well as end-of-pipe technology. This development was the initiator for spinning out QUILL from QUESTOR.

INTERDISCIPLINARITY

One of the defining features of an I/UCRC and certainly of QUESTOR is interdisciplinarity. QUESTOR started out with five disciplines involved and now has seven. Thus research projects are often, indeed mostly, submitted to the Centre by two or more academics from different schools within Queen's. Apart from the funding attracted to the University this has been one of the most valuable outcomes as far as University management is concerned. Implementing this shift in attitude in academics was not easy and to do so it was necessary to change the way credit for obtaining research funds was allocated within and across the Faculties so that two or more academics could each have a share of the credit rather than one "PI" getting all the credit as before.

This interdisciplinarity is not restricted to traditional science and engineering disciplines as might be expected. Within QUESTOR there have also been psychology projects relating to environmental communication and these were suggested by the Members and strongly supported by them. A good example of a cross-disciplinary research project was a real site remediation project that involved chemists, chemical engineers, microbiologists, civil engineers and psychologists who studied the communication of the work to the surrounding population.

KNOWLEDGE AND TECHNOLOGY TRANSFER

The I/UCRC model is one of the most effective mechanisms for achieving knowledge transfer from the university to industry. This occurs by two main routes; a) students and staff trained on highly relevant projects and in frequent contact with industry members are ideally equipped to move into good posts in industry taking their knowledge with them; b) industry members interacting with the Centre learn of state of the art advances sooner than they would otherwise and take them back to the company with them.

The process of technology transfer is greatly facilitated by the modifications to the model described above, for example, the ATU acts as a technology translator between the Centre and the Members and also client companies that are not Members. Thus the process is not totally reliant on technology pull from the Members. In addition, QUESTOR Technologies Ltd., by commercializing research carried out in the Centre, also acts as a very effective technology translator.

OWNERSHIP BY THE MEMBERS

A second defining feature of QUESTOR is the way the constructive relationship between the Members and the Centre has flourished. An example of this is the way that the Members approved the formation of the QUESTOR ATU and also QUESTOR Technologies Ltd. The Members as well as the Centre management believed that these developments would benefit the Centre and of course eventually the Members as well. This relationship was no accident. From the start the Members were treated as honoured guests in the University, for example the IAB meetings were held in the Council Chamber, the most prestigious venue in the University. Members were assured that they had full control of the research agenda of the Centre and while this was not too popular with many academics it was strictly adhered to. Those academics that were unhappy were advised to seek funding for their research projects from another source. All of this led to the Members developing an ownership of the Centre, in other words, QUESTOR was their Centre as well as Queens' Centre and this led to many acts of generosity by various Members, for example, donating chemicals, equipment and their time to help the Centre grow and be successful.

When the Centre won the Queen's Anniversary Prize in 1997 the Chairman of the IAB attended the award ceremony in Buckingham Palace and when the Secretary of State for Northern Ireland laid on a reception in honour of the award the majority of the Members turned up to support "their" Centre.

EVALUATION

QUESTOR has been very fortunate to be included in the NSF Centre evaluation programme since 1992. The Centre performed very well against the norms for the US centres and this proved to be a most valuable recruitment tool, allowing prospective Members to be assured the administration of the Centre was as robust as the research, which they could assess for themselves.

CONCLUSIONS

The US national Science Foundation model for industry university cooperation is an excellent mechanism for training postgraduate students and postdoctoral staff in science and engineering. It has particular relevance in the water treatment field due to the need for an interdisciplinary approach to the challenges. The model as applied in Northern Ireland encourages and facilitates knowledge and technology transfer from the university to industry through a variety of very effective mechanisms. The successes of the QUESTOR and QUILL Centres in Queen’s University have demonstrated that the model is very suitable for transfer to other countries.

REFERENCE

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WESTCOUNTRY RIVERS TRUST UNITED KINGDOM: A PIONEERING PROGRAMME FOR RESTORATION AND REGENERATION OF MAJOR RIVER BASINS

R.J. Stollard and A. Rickard

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INTRODUCTION

Westcountry Rivers Trust (UK) was established in 1995 to pioneer a new approach for restoration and regeneration of major river basins with the focus initially on the Tamar River in the counties of Devon and Cornwall, UK. Due to the geomorphology of this region the communities' water supplies are dependent on surface waters. In addition with the substantial tourism and seafaring activities and important fishing and shellfish industries there is a need to ensure that the environment and water quality of the rivers, estuaries and beaches are sustained to the highest standards.

However, within this predominantly agricultural area, changes in land use such as farm management and cropping patterns, fertilizer usage and combined drainage operations over the last 30 years have resulted over time in widespread habitat destruction, degradation and pollution, affecting the water resources and associated species diversity and density within the region. The Tamar River was identified as one of the worst affected.

The ultimate aim of the Tamar 2000 Support Project was the testing, proving and delivery, at a modest cost, of an approach to sustainable land and river use, which is transferable to other river catchments that drain agricultural areas in the UK and elsewhere. This is achieved by the unique holistic and collaborative approach that encourages land owners/users to make changes to their current management techniques together with education and training in new techniques that not only financially benefit farmers and

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landowners but simultaneously benefit the whole community and the regional economy and environment.

Following the success of the Tamar River Support Programme and the development of four other similar trusts, the Association of Rivers Trusts (ART) was established in 2001, and further Trusts throughout the United Kingdom are being developed. Close association has been nurtured with many other key bodies such as the Salmon and Trout Association, the Atlantic Salmon Trust, the Scottish Fishery Trusts and the Environment Agency. Further collaborative projects with other European countries are also currently being established.

TAMAR 2000 SUPPORT PROJECT

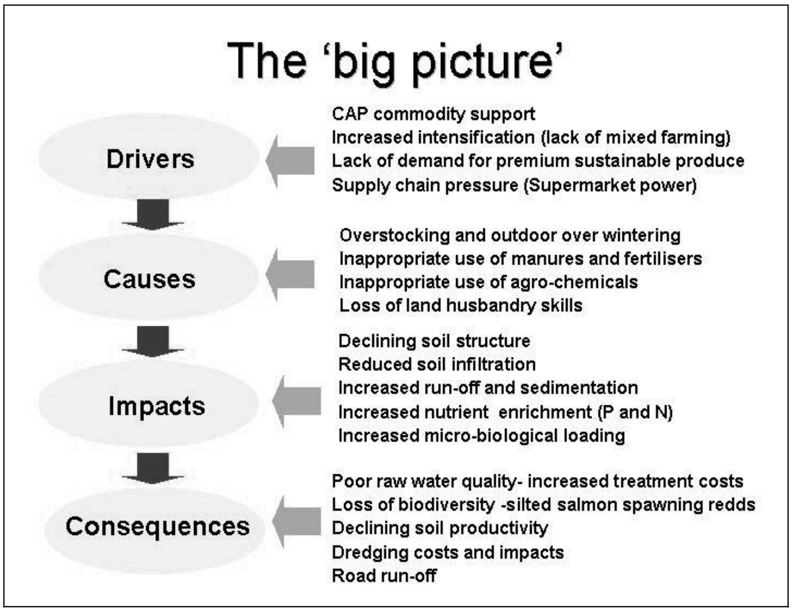
Project Description

The Tamar 2000 SUPPORT Project is a pathfinder project that works closely with farmers, riparian owners and the wider community to develop sustainable catchment land management practices, which aim to conserve and restore environmental quality for both people and wildlife while delivering economic gains. This is achieved in particular by optimizing farm inputs, employing best management practices and the management and restoration of key river and wetland habitats with benefits to water quality, fisheries and other wildlife, linked to recreation and tourism development. Not only does this result in safeguarding existing jobs, but also new employment opportunities, created through new enterprise, arise and both the water supplies and the economy of the region as a whole are protected and improved. Measures are applied that: (i) reduce erosion and the sedimentation of salmonid spawning gravels, (ii) reduce diffuse pollution and improve river water quality, (iii) conserve and restore wetlands and their functions, (iv) restore river corridor habitats, and (v) sustain local communities that maintain the river.

The Problems

Fig. 1 summarizes the key agricultural influences that over many years have led to the deterioration in the water quality and sustainability of the river basin, and Fig. 2 highlights the wider consequences of this deterioration.

There was an urgent need to redress these consequences and to restore and regenerate the river basin environment whereby management practices would provide a balanced and sustainable water quality environment.



The 'big picture'

Drivers

CAP commodity support
Increased intensification (lack of mixed farming)
Lack of demand for premium sustainable produce
Supply chain pressure (Supermarket power)

Causes

Overstocking and outdoor over wintering
Inappropriate use of manures and fertilisers
Inappropriate use of agro-chemicals
Loss of land husbandry skills

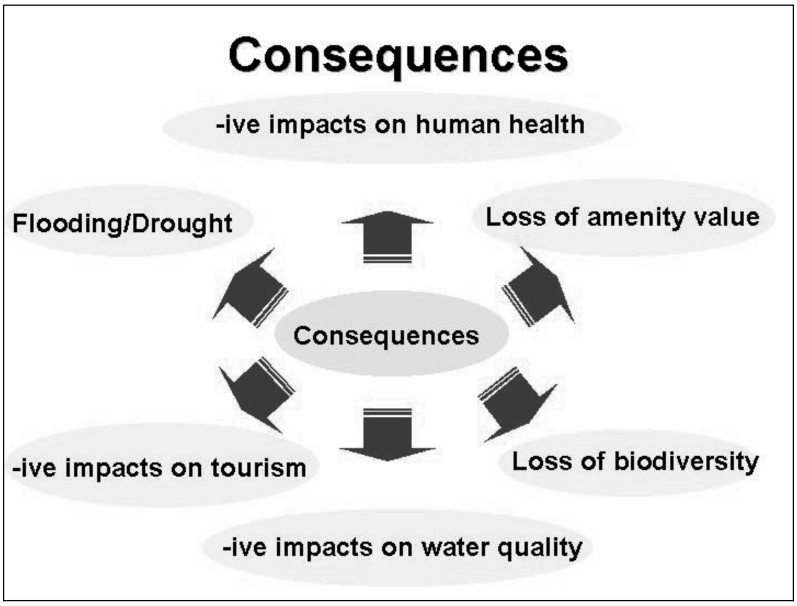
Impacts

Declining soil structure
Reduced soil infiltration
Increased run-off and sedimentation
Increased nutrient enrichment (P and N)
Increased micro-biological loading

Consequences

Poor raw water quality- increased treatment costs
Loss of biodiversity -silted salmon spawning redds
Declining soil productivity
Dredging costs and impacts
Road run-off

Figure 1. Deterioration in river basin and water quality due to agricultural influences.



Consequences

-ive impacts on human health

Flooding/Drought

Loss of amenity value

Consequences

-ive impacts on tourism

Loss of biodiversity

-ive impacts on water quality

Figure 2. Economic and environmental consequences of river basin deterioration.

An Innovative, Holistic Approach

Previous attempts to restore environmental quality have frequently failed because they have lacked a catchment scale, they have not integrated sectoral interests and most important have not engaged fully the local people. Tamar 2000 adopted an innovative, holistic approach featuring the integrated application of proven best land use practice whereby the land owners in the catchment are supported with a combined package of advice, training and finance. The project provides a coordinated, integrated, large-scale, practical and on-going demonstration of what can be achieved by applying techniques that have already been tried and tested on a smaller scale, such as the use of riparian or wetland areas for improvement of water quality, combined with reductions in the use of fertilizers and pesticides. Very long sentence above integrated farm and river based management plans are being coupled with a series of support measures, which include buffer zones, wetland recreation, tree planting and funds for riverbank fencing.

A Collaborative Approach

This innovative project coordinated by the Westcountry Rivers Trust is delivered in partnership with the Wetland Ecosystems Research Group – WREG (part of the Royal Holloway Institute for Environmental Research, University of London) and other relevant locally based organizations.

The initial 4 year project, concluded in June 2000, received around half of its funding from a combination of UK Government and European Union sources, under EU Objective 5B, EAGGF Measure 5.1. The Westcountry Rivers Trust secured the remaining funding from charitable trusts, company sponsorship and other private contributions.

The combined knowledge and expertise of the partnership organizations and individuals has been offered to farmers and landowners in the catchment. Through this education and assistance in using new skills in conservation, pollution control, habitat improvement and alternative methods of production, land owners have become aware of and are able to apply the best river restoration methods available and jointly create management strategies which are both cost efficient and sustainable. Additionally the subsequent wise use of riparian habitats and the benefits of integrated plans covering all land operations are being demonstrated.

Integrated Land-Water Management Plans

Experienced field advisors are trained actively in the best practices and free field visits by the advisors are offered to land owners with the objectives of jointly reviewing the land use and potential for environmental and economic improvements. Site-specific management plans are developed, integrating best practices associated with the land uses and an appraisal of options to improve land use, reduce costs, improve returns and meet specific conservation needs. This is worked up into an integrated catchment study of potential and priority work. Ultimately this will ensure site-by-site evaluation on a holistic basis and allow catchment scale identification of problems and benefits to ensure integrated solutions. Land owners are encouraged to undertake any necessary work on their own land themselves, and financial support is provided where necessary from either programme funds or from grant aiding agencies.

Wetlands

Recognition of the significance of the role of wetlands in the maintenance and improvement of environmental quality is rapidly increasing and is seen as a key factor for environmental restoration. The use of wetlands as 'buffer zones' is also increasing, but the capacity of wetlands to perform these functions varies depending on many variables, including their type and location. It is believed that the degradation and loss of wetlands is a major contributor to many of the environmental problems that exist in river catchments today. It is predicted that the maintenance, re-establishment and use of wetlands within the catchment will result in mitigation of many of the adverse effects of current agricultural practices, as well as enhancement of the environment as a whole. A significant amount of scientific evidence exists as to how they can be effective in the enhancement and maintenance of environmental quality and the input from WERG in this respect provides important details on this aspect.

WERG's development of a set of procedures for the functional analysis of wetlands funded by the European Community (DGXII) benefits such projects. It allows assessment of functions such as flood alleviation, recharge and discharge of groundwater, nutrient removal (particularly nitrate) from surface and ground waters and the maintenance of wildlife habitats, biodiversity and support of food webs. However the performance of these functions is often impaired through both historical and present day land reclamation and drainage, or more insidious processes such as distant groundwater abstraction or pollution. Through the identification and mapping of wetlands within the Upper Tamar catchment it has been possible to assess their status and functional capacity. Fig. 3 illustrates the mapping of the upper Tamar drainage and wetland areas.

The Tamar had a record of failure to meet water quality objectives and this may have been due in part to the progressive loss of river marginal wetlands in the catchment. Identification of the specific environmental impacts such as excessive sediment loading and diffuse pollution allows the

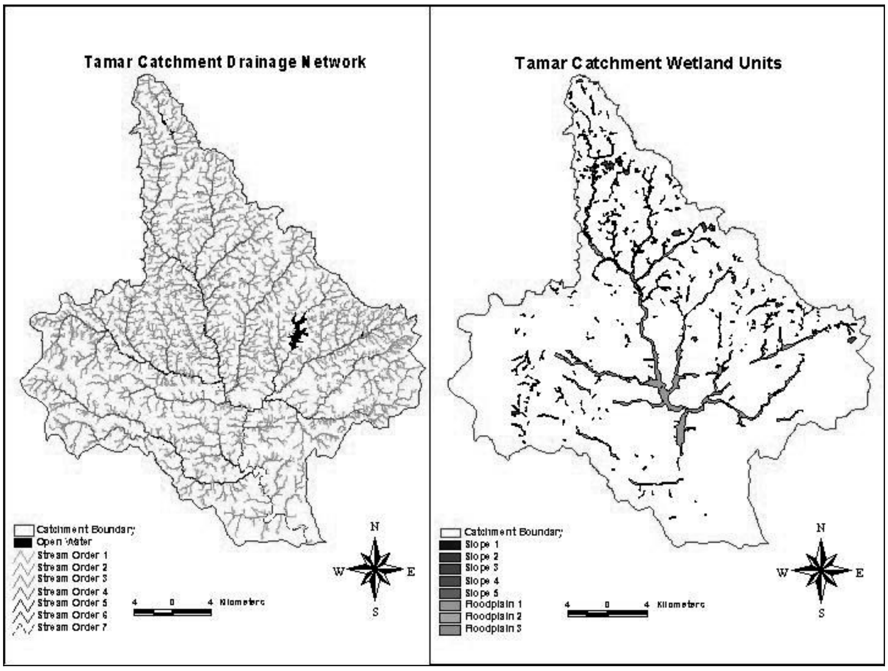


Figure 3. Illustration of the mapping of the upper Tamar drainage and wetland areas.

recommendation of appropriate land use policies and practices, and the targeting of wetlands to perform specific functions at suitable locations. It is important to be aware that not all wetland functions are compatible. For example, the use of a wetland for the improvement of water quality in nutrient enriched surface water is likely to result in the loss of specialized habitat such as acidic heath and bog communities through the succession of more eutrophic assemblages. Therefore the environmental requirements at specific locations must be determined before management policies are implemented. Additionally, local hydrology is examined prior to the establishment of buffer zones. Recent work has shown that the most effective buffer zones with regard to nutrient removal sometimes occur not along the river channel, but along drainage ditches which may be some distance from the main river channel. By targeting the most productive zones with regard to the function that is to be performed, not only will more effective environmental protection be carried out, but also cost efficiency is optimized.

Demonstration Sites

One of the main ways to illustrate how landowners can make improvements is through the establishment of a number of demonstration sites. At these locations land management plans are established incorporating different land use, buffer zone location and where applicable wetland management techniques. The nature of these management techniques depends upon the specific requirements of the location, and these in turn are related to the site-specific problems identified. Following a period of monitoring at these locations they are used for teaching and training landowners from other areas such that the findings and techniques employed in the project can be utilized by landowners in other regions.

Action on the Ground

An important aspect of the project is the way in which it tackles the causes, not just the symptoms, of decline in water quality and habitat. Improvements brought about by the project are also designed to be sustainable. To achieve these aims it is crucially important to fully engage with landowners and/or farmers within the wider catchment and to be able to demonstrate delivery of economic savings and gains to farmers within the project's holistic farm plans. Management of fertilizers and farmyard manures being a case in point.

A considerable number of farms in the project are able to identify savings of 20% on nitrate fertilizer usage. The savings come from careful targeting, timing and application of bag fertilizer and the application of correct values to soil N and organic manures in the crop requirement calculation. Coupled with the use of clover in suitable grass leys and focused cropping, grazing and cutting regimes, benefits accrue to both farm profitability and the environment. The substantial cash savings on fertilizer are equivalent to that which previously would have leached from the soil and contributed to the excess nutrient enrichment of the river.

Farmyard manure, slurry and dirty water suffer from being often referred to as farm waste. This regularly means farmers underestimate its nutrient value as well as the costs associated with its storage and application. Here the project seeks to attach real values to this important farm by-product and reduce handling costs by waste minimization techniques. In particular concentrating effort on clean and dirty water separation in the farmyard. Advice is then directed to its careful application to reduce run off and maximize take up by the growing crop.

Phosphates have perhaps played a bigger part than nitrates in the eutrophication problems associated with rivers and reservoirs. As with nitrates soil testing has revealed that on many livestock farms the application of bag phosphate can be dramatically reduced or even cut out altogether. This work coupled with developing Best Management Practices to reduce loss of topsoil and erosion (phosphates often enter the river attached to soil particles) brings further gains to both farmer and water quality.

Habitat Restoration

The maintenance and restoration of key wetlands coupled with the development of buffer zones and the re-vegetation of ditches within management plans also play an important role in trapping sediment, nutrient stripping and de-nitrification. Work indicates that the added water storage provided by these wetlands and ditches will offer measurable benefits in the amelioration of flashy flows and reduction of the extreme conditions brought about by flood and drought.

Every bit as important and visibly the most spectacular are the habitat improvements brought about by fencing livestock out of the river corridor particularly when coupled with river corridor management in the form of coppicing and /or tree planting. The before and after photographs in Fig. 4 of river corridor restored in this way are compelling evidence of the way in which this vital habitat has been neglected and abused in the past.

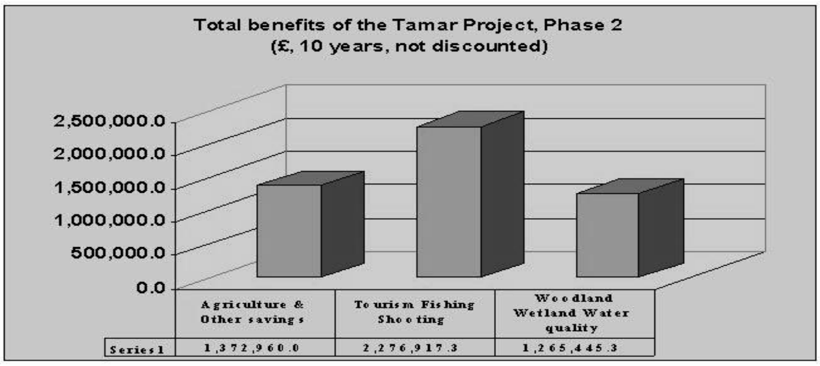
Figure 4. River corridor recovery after exclusion of livestock.

Farmers too have been quick to see the advantages to the husbandry of their livestock through fencing off the river in this way and again with the provision of alternative drinking areas such as pasture pumps, can measure the benefit in cash terms.

Monitoring, Evaluating and Reporting

An overall monitoring and evaluation process has been developed for assessing improvements within the catchment. This comprises the assessment of key economic, physical, chemical and natural features during the project. The results of implementation of the management plans are evaluated by: (i) changes in land use and restoration of habitat, (ii) benefits to the aquatic environment, and (iii) economic benefits related to the changes of use of the surrounding land.

The Academy of Economic Studies, Bucharest and the Royal Holloway Institute have prepared an independent detailed evaluation of the economic benefits of the Tamar 2000 Project for Westcountry Rivers Trust for Environmental Research. This focused primarily on those related to the community within the catchment area, while evaluation of the wider benefits associated with improved quality of water extracted from the river basin for other uses was considered to be underestimated.



BENEFIT/COST RATIO	**DIRECT Benefit/ Cost**	**INDIRECT Benefit/ Cost**	**TOTAL Benefit/ Cost**
without discounting	4.3	3.9	8.2
with discounting (6%)	3.4	3.0	6.4

Figure 5. Analysis of economic benefits over a ten-year period.

Fig. 5 summarises the benefits into three categories; agricultural and other savings; tourism, fishing & shooting; and woodland and wetland water quality. Approximately 50% of the benefits came from increased tourism, fishing and shooting reflecting both development of new enterprises and enhanced environmental provisions and over a ten-year period the estimated benefit to cost ratio without discounting was calculated to be 8.2.

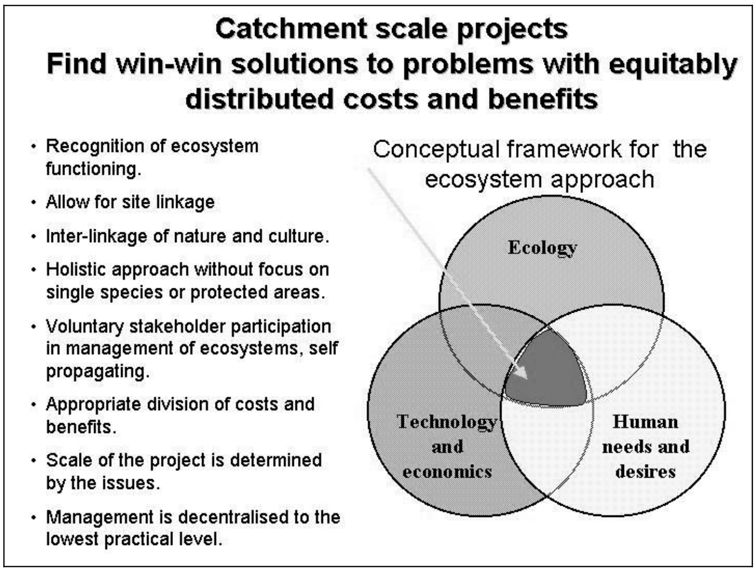
To date, the Tamar 2000 project's reception and outputs have exceeded expectation. Landowners/farmers have responded better than anticipated to the project's approach. Optimizing inputs, providing one of the few ways to improve profitability without the need for large investment in particular, has stimulated action by farmers. Similarly the opportunity to improve capital values has provided an incentive to many. Some farmers have also used their participation in the project and their farm management plans when negotiating with their bank. Project meetings have also taken place with NFU Insurance regarding farm pollution risk assessment and the potential risk reduction as a result of the implementation of farm management plans and Best Management Practice. A larger than expected number of farmers has also grasped the opportunity to diversify into tourism or to add value to existing operations. Of key importance has been the continued improvement of the water quality and sustainability of the environment of the Tamar River basin for the benefit of all. Key factors in the success of the project include: (i) strong working partnerships, (ii) combining skills and resources, (iii) catchment scale based approach, (iv) the adoption of a voluntary approach rather than regulation, (v) providing advice and supporting plans that are non-prescriptive, (vi) adopting a practical approach that involves the farmer and incorporates their vision, (vii) a strong one-to-one relationship between advisor and farmer. (viii) linking economic gains to environmental improvements, and (ix) in terms of environmental improvement, tackling the causes as well as the symptoms of decline.

OUTCOMES

The delivery of the Tamar 2000 project has achieved substantial environmental, physical and economic outputs. Importantly, as a pathfinder project the design, delivery and recording systems are now performing well after refinement and there is great scope (and demand) for transferability of this approach to other river catchments. Fig. 6 summaries the key features for programme delivery based on an ecosystem approach.

Central to success is having the management of activities decentralized to the lowest practical level yet operated on the principal of "thinking globally and acting locally". Only by engaging with the owners and managers of the river's resources can integrated land and water management be achieved throughout the river basin. Two guiding principles of such programmes are: (i) significant steps towards sustainability of actions can be made by "helping a lot of people to each achieve a little" and (ii) subtle management changes, when sufficiently widespread, will reach a critical mass within a river's catchment area.

Westcountry Rivers Trust are now operating schemes covering many other river basins within Devon and Cornwall, SW England having secured further European funding especially for Cornwall.



Catchment scale projects
Find win-win solutions to problems with equitably distributed costs and benefits

- Recognition of ecosystem functioning.
- Allow for site linkage
- Inter-linkage of nature and culture.
- Holistic approach without focus on single species or protected areas.
- Voluntary stakeholder participation in management of ecosystems, self propagating.
- Appropriate division of costs and benefits.
- Scale of the project is determined by the issues.
- Management is decentralised to the lowest practical level.

Figure 6. Key features of the Ecosystem approach to catchment scale projects.

A further important feature of the activities of Westcountry Rivers Trust is to maintain close contact and involvement with on-going relevant research projects and to keep abreast of new techniques and technologies. An important aspect of their work is riparian studies. The rivers of South West England are important strongholds for salmonids, which have been declining in numbers in recent years. The Trust has executed several multi-million pound catchment scale projects where the Atlantic salmon and other salmonids are regarded as key indicators for project targeting and one of a range of indicators of project success. The Trust has collaborated with many organisations during these projects including the Environment Agency, the Atlantic Salmon Trust, the Scottish Fishery Trusts, and the Salmon & Trout Association. The Trust's science team is currently supervising a PhD student studying the population genetics of wild Brown Trout on the River Dart in Devon and the implications for stock management.

More recently, other Trusts have been developed to carry out similar programmes for river basins in other areas of the United Kingdom. Most rivers trusts combine the use of best available science and data drawn from the Environment Agency and by employing their own scientists, supported by volunteers and riparian owners in each catchment or river basin. This structure is typified by a Board of Trustees that "head up" and oversee the Trust, freely offering their time and a wealth of knowledge covering important aspects of Trust activity including legal, business and accounting, fisheries, agriculture, tourism and education. Where funds permit the Board will usually appoint a small team of professionals, often beginning with a Scientist or Educationalist. As the Trust develops so the team may be expanded to include other specialists including a Manager or Director who will undertake the day to day running of the Trust and its projects. This team will then work very closely with the wider community including the river owners and managers.

As one might expect, their formation is in response to the growing awareness of the wider environment or concern over the decline of certain key indicator species, decline in water quality, notable pollution events and the recognition of the need to restore the rivers. Most trusts, where eligible, have successfully applied for European Union structural funds such as LEADER, Objectives One, Two and 5b or Lottery funds and obtained from various sources additional match funding including some from Government agencies. From a Government fund-holders position, partnerships like this can provide a very cost-effective conduit for delivery of environmental, social and economic outputs demonstrating strong community stakeholder involvement.

ASSOCIATION OF RIVERS TRUSTS – “ART”

During 2001, spearheaded by Westcountry Rivers Trust, the Eden Rivers Trust, Tweed Foundation, Westcountry Rivers Trust and Wye & Usk Foundation publicly announced the launch of an “Association of River Trusts” (ART) for England and Wales. The need for such a body is a logical extension of the increasing level of liaison that had taken place for some time between established rivers trusts. However the speed with which the new organisation has become recognised and the demands already placed upon it by new and emerging trusts seeking assistance could hardly have been anticipated. A further six Trusts are at various stages of development.

ART Aims and Objectives

The main aims of the Association of Rivers Trusts are: “to co-ordinate, represent and develop the aims and interests of the member Trusts in the promotion of sustainable, holistic and integrated catchment management and sound environmental practices, recognizing the wider economic benefits for local communities and the value of education.”

The key principles of ART are based on: (i) consent, (ii) subsidiarity - where ART will serve its members and decisions will be taken at the appropriate level, (iii) partnership, and (iv) education and technology transfer - with particular reference to new and emerging trusts and collaborative programmes.

The Rivers Trust movement is a bottom up grassroots development, initiated by a number of different community groups from around the country, working independently to form Trusts. The formation of ART is simply a natural response to mature trusts wishing to share information and work more closely together to help others and provide synergy.

Improving the riverine corridor and surrounding catchment is a complex process involving Government Departments, its Agencies and many other diverse organizations. ART provides an important link between the established, and the new and emerging Rivers and Fisheries Trusts. It also provides a forum to develop ideas, best practice and policy guidance and test transferability. Furthermore it offers a national platform for regional Trusts to "showcase" their work and to inform and enthuse others, giving advice and encouragement and ultimately, empowerment. ART is currently coordinating programmes looking at all relevant aspects for the sustainability and improvement of salmon and trout fish stocks around the whole country.

Legislative Pressures for Change

ART has a key role to play in ensuring that the European Union legislative directives for change in water management are met and also in providing collective feedback for future deliberations on EU policy. There are eight important directives, which all EU countries are currently having to address: (1) Groundwater Directive, (2) Nitrates Directive, (3) Habitats Directive, (4) Bathing Water Directive, (5) Farm Waste Directive, (6) Water Framework Directive, (7) Agenda 2000/ERDP, and (8) Freshwater Fish Directive.

With the importance of the global sustainability of good quality freshwater supplies and the increasing importance of European Union legislation, ART has also established relationships with similar interested bodies in other European countries with a view to collaboration and further development of projects and new methods for environmental sustainability of our rivers and also for widening the opportunity to secure additional European funding and support for new programmes.

CENTRE OF EXCELLENCE

As a result of their extensive work Westcountry Rivers Trust has developed a series of very comprehensive "Best Practice" technical manuals on all aspects of river restoration, regeneration and sustainable land use and agricultural management practices including: (i) water, (ii) soils, (iii) organic manures, (iv) fertilizers, (v) chemicals and pesticides, (vi) energy usage, and (vii) bio-diversity.

The Trust is also planning to establish a “Centre of Excellence” based on Sustainable River Basin Management for continued research, development and wider educational activity to promote and encourage the successful methodologies that they and other bodies have created.

SUMMARY

The pioneering programme for the restoration and regeneration of River Basins spearheaded by Westcountry Rivers Trust and expanded through the Association of Rivers Trusts, together with future collaborative programmes involving other European countries, can positively influence the environmental sustainability of good water supplies within river basins and thereby the important extraction and provision of potable water supplies for human consumption.

RECENT DEVELOPMENTS IN WASTEWATER TREATMENT IN CONSTRUCTED WETLANDS IN POLAND

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ABSTRACT

Nowadays, more than 100 constructed wetlands are in operation in Poland. Most of them are one-stage wetland systems with horizontal subsurface flows. Such constructed wetlands ensure efficient removal of organic matter (BOD_5, COD_{Cr}) and suspended solids, but the efficiency of removal of nitrogen compounds in many cases is insufficient. In the period from 1995 to 2003, measurements of removal of contaminations in 11 household pilot units and 4 community plants equipped with one-stage horizontal flow beds, as well as in 4 community plants equipped with hybrid reed wetland systems composed of HF-CW (constructed wetlands with horizontal flow) and VF-CW (constructed wetlands with vertical flow) filters, were carried out. It was found that sufficient removal of organic matter (70-90 %) took place in the HF filters. The removal of nitrogen took place in VF beds and HF beds (denitrification) applied as a second and third stage of primary hybrid treatment. The removal of nitrogen was limited by the efficiency of the nitrification process in VF beds in wetland systems.

INTRODUCTION

In Poland, almost all farms are provided with water from central water supply systems or from individual wells. However, only 8.2 % of the farms are equipped with sewerage systems. Central wastewater treatment plants (WWTP) cannot provide an adequate solution to this problem due to the scattered location of the farms. Also, water consumption in rural areas is substantially smaller than in cities. Usually, it ranges from 50-100 L/day as

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compared to 150 L/day in cities. Therefore, the resulting wastewaters are more concentrated and are more difficult to treat in conventional systems.

In the last decade, more than 100 constructed wetland systems were built in Poland. Most of them are one-stage systems with horizontal subsurface flow, which are fed with sewage after mechanical pre-treatment. Unfortunately, lack of sufficient knowledge and improper maintenance resulted in low efficiency, especially for removal of nitrogen compounds.

Until 2002, all Polish standards were equal and obligatory in all instances where the amount of sewage exceeded 5 m^3/day. This means that sewage generated in a small town or village had to be treated with the same efficiency as in larger city. Organic matter expressed in terms of BOD should not have exceeded 30 mg O_2/L, whereas nitrogen concentrations in sewage discharged to surface waters and soil had to be < 30 mg/L and < 6 mg/L in terms of total nitrogen, N_{tot}, and ammonium NH_4^+, respectively. The standard pertaining to the ammonium concentration was especially difficult to comply with in rural regions (Regulation 1999).

New Polish standards implemented in 2002 created better conditions for development of constructed wetlands. Since December 1, 2002, discharged sewage from 50-2000 people (the majority of constructed wetland in Poland) has to comply with the following standards: $BOD_5 \leq 40$ mg O_2/L, $COD_{Cr} \leq 150$ mg O_2/L, suspended solids (SS) ≤ 50 mg/L. If the outflow is discharged to a lake, additional criteria for nutrients are set as follows: $N_{tot} \leq$ 30 mg/L, total phosphorous $P_{tot} \leq 5$ mg/L (Regulation 2002). These alleviated requirements seem to be more realistic and constructed wetlands ensure efficient removal of suspended solids and organic matter. Also, effective nitrogen removal is possible in systems containing at least two beds with horizontal and vertical flow placed as the second and third biological step. These systems exemplify so-called hybrid systems.

The removal of contaminants in several HF-CWs in pilot individual and community systems, as well as in primary hybrid horizontal/vertical flow systems, introduced within the last seven years, is presented in this paper.

METHODS

One-Stage Constructed Wetlands

Out of 11 constructed wetlands (CW) built for individual farms, 4 were located near Lublin, 3 were near Ostroleka and another 4 were near Ciechanow in the Mazowsze region. The systems located near Lublin and Ostroleka were constructed under the UNEP WHO and Polish Ministry of Environmental Protection Natural Resources and Forestry Programme "Sanitation of rural areas and proper agricultural practices" (Obarska-Pempkowiak et al. 1997). Averaged samples of sewage subjected to mechanical separation were taken once or twice a month for three years before and after treatment in CW systems. The sewage quality was assessed by monitoring physical and chemical parameters, such as temperature of sewage and air, total suspended solids, BOD_5, COD_{Cr}, ammonium (NH_4^+), nitrate, nitrite, organic nitrogen, total phosphorus, and phosphates. Total nitrogen was estimated as a sum of the nitrogen components in all analysed forms. In all samples, measurements were performed according to Standard Methods.

The systems near Ciechanow were designed and implemented by the Institute of Building, Mechanisation and Electrification of Agriculture in Warsaw. The major characteristics of the beds in these systems were as follows: (i) the area of the bed was based on a surface area per capita loading of 4.5 m^2/person, which means that the specific surface loading of a bed was approximately 29 mm^2/day, (ii) the length of the bed L=20 m at all plants, (iii) the width W of the beds was variable, depending on the number of persons, e.g. W = 1, 1.1, 1.3, and 1.5 m for 4, 5, 6, and 8 people, respectively, (iv) the average depth of the bed of individual systems was 1 m, and (v) the slope of the bed bottom was 1%.

The filter systems located near Ostroleka and Lublin, numbered from 1 to 7, were filled with medium grain sand, whereas systems I, II and IV located near Ciechanow were filled with a mix of gravel (grain size 0.5 – 8 mm) and artificial aggregate “Pollytag” (grain size 4-8 mm). “Pollytag” is produced from flue dust containing approximately 58 % SiO_2, 22 % Al_2O_3, 1.4 % Mg and 0.3 % S. The porosity of the granules is about 40 %. Usage of “Pollytag” aggregates as a filter material increased the retention time, sorption capacity of the beds and ability to bind toxic substances. One filter bed (III) was filled with coarse sand (grain size 0.1-3 mm). The general characteristics of the pilot farm wastewater treatment plants in the villages in Poland are given in the Table 1.

Four local community HF-CWs located near Gorzow Wielkopolski were investigated by Sadecka (2001) during seven years of operation. The characteristics of these systems are presented in Table 2. The flow rate of sewage was in the range 26.3 – 90.0 m^3/day. These systems were constructed at the beginning of the 1990s without sufficient knowledge about their properties and design. Averaged samples of sewage were collected once a month. The measurements were carried out similarly to individual systems.

The removal efficiency in individual and community systems was calculated by the formula $\eta = (C_0\text{-}C)/C_0$, where C_0 and C are the input and output concentrations of contaminants, respectively.

Table 1. Characteristics of individual farm HF-CWs near Lublin, Ostroleka and Cichanow.

System	Name of the farmer	Number of persons	Characteristics of beds		
			Area	Plants	Filter material
Lublin Voyevodship					
1	Olejnik	9	45	Willow	Medium sand
2	Próchniak	6	50	Willow	Medium sand
3	Chołaj	7	38	Willow	Medium sand
4	Podstawka	7+10 in summer season	50	Willow	Medium sand
Mazowsze Voyevodship					
5	Kesler	6	60	Willow	Natural soil, mainly (85% medium sand)
6	Shiffer	5	35	Reed	Natural soil, mainly (75% coarse sand)
7	Łysakiewicz	6+15 in summer season	35	Reed	Natural soil, mainly (75% coarse sand)

Przymorze village near Ciechanow, Mazowsze Voyevodship

System	Name of farmer	Number of persons	Characteristics of willow bed				
			Area [m^2]	Plants	Shape, size L×W [m]	Substrate material	k_{10}^{**} [m/d]
I	Antczak	6	27.0	Willow	"U" (2×10) ×1.3	Mix (gravel & Pollytag) $U^{*}=3.4$	650
II	Kuc	4	18.0	Willow	Rectangular 18×1.0	Mix (gravel & Pollytag) $U^{*}=3.4$	650
III	Grzegorz Wikliński	5	22.5	Willow	"U" (2×10) ×1.1	Coarse sand $U^{*}=2.6$	100
IV	Tadeusz Wikliński	8	36.0	Willow	"U" (2×10) ×1.5	Mix (gravel & Pollytag) $U^{*}=3.4$	650

[*] $U = d_{60}/d_{10}$ – grain uniformity coefficient, where d_{60} is grain size for which 60% of grains are finer and d_{10} is the grain size for which 10% of grains are finer.

[**] k_{10} is the hydraulic conductivity estimated using, according to the Polish Standard, the Hazen formula $k_{10}=Cd_{10}^2$, where C is the empirical coefficient dependent on porosity.

Table 2. Characteristics of local communitie's HF-CWs near Gorzów Wielkopolski.

WWTP	Flow, m^3/day	Area, m^2	Depth, m	Specific area m^2/person
Wawrów	90.0	3500	0.8	2.7
Gralewo	46.3	3325	0.9	3.0
Małyszyn	26.3	4800	0.4	4.0
Rokitno	45.0	1200	0.4	10.0

Hybrid Wetland Systems

Studies were carried out at three constructed hybrid wetlands in Darżlubie, Sarbsk and Wiklino near Slupsk in the Pomeranian Region, as well as in Sobiechy in the Podlaski Region. After mechanical pre-treatment, the sewage was pumped into a biological treatment unit consisting of HF-CW and VF-CW beds. In the system located in Sarbsk, the sewage outflowing from the VF-CW bed was recirculated. In the Wiklino system, an additional HF-CW type II bed was constructed. All systems were inhabited by reeds.

The characteristics of these systems and the configuration of the beds are given in Table 3. Sewage samples in Darżlubie were collected once per week during the period 1994-1996 (Darżlubie I - before colmatation) and in 1997-1999 (Darżlubie II - after colmatation) (Obarska–Pempkowiak 1999). Colmatation, i.e. the increased concentration of suspended particles in the pore volumes of the stream bed, which results in reduction of the permeability of the liners and decrease of removal efficiency, of the first HF-CW bed occurred in 1996 and was caused by overloading of the system by animal sewage supplied from individual farms. The samples were collected in Wiklino during the period 1998-February 2000 (before modernisation) and from March 2000 till present (Wiklino II - after modernisation).

In spring 2000, modernisation of the system supplying sewage into the VF-CW bed was completed only in Wiklino. Due to installation of a pump, periodical inflow of sewage into the single unit of the VF-CW bed became possible. Periodical dosing of sewage resulted in better aeration of the bed (Gajewska and Obarska-Pempkowiak 2001).

RESULTS AND DISCUSSION

One-Stage Constructed Wetlands

The BOD_5 loading in pilot individual plants near Lublin and Ostroleka in the first year of operation ranged from 1.21 to 5.76 g O_2 $m^{-2}day^{-1}$. The loading of COD ranged from 2.79 to 9.06 g O_2 $m^{-2}day^{-1}$ with the exception of plant No. 7, where it was 18.06 g O_2 $m^{-2}day^{-1}$. The loading of organic nitrogen was higher in the Ostroleka region and varied from 0.31 to 0.72 g $m^{-2}day^{-1}$, while in Lublin region it ranged from 0.09 to 0.17 g $m^{-2}day^{-1}$. The total phosphorus loading in the plants investigated ranged from 0.09-0.47 g m^{-2} day^{-1}.

Sewage generated in farms Nos. 1, 2, 3, and 5 was similar to municipal sewage. Average water consumption in these farms was equal to 55 litres per person. The remaining farms produced sewage, which is typical for agricultural activities, and the average water consumption was 120 litres per person (Sikorski 1997). The lower concentration of organic matter in septic

Table 3. The characteristics of constructed wetland hybrid systems.

WWTP	Flow, m^3/day	Configuration	Area, m^2	Depth, m	Specific area, m^2/person
Wiklino I- before modernisation	18.7	HF	1050	0.6	7.0
		VF	624	0.4	4.0
		HF	540	0.6	3.4
			Total 2 214		Total 14.4
Wiklino II- after modernisation	18.6	HF	1050	0.6	7.0
		VF	624	0.4	2.0
		HF	540	0.6	3.4
			Total 2 214		*Total* 12.4
Sarbsk *	29.7	HF	1610	0.6	8.5
		VF	520	0.5	2.6
			Total 2 130		*Total* 9.1
Darżlubie I- before colmatation	170	HF-CW I	1200	0.6	1.6
		Cascade filter	400		
		HF-CW II	500	0.6	0.5
		VF-CW	250	1.0	0.7
		HF-CW III	1000	0.6	1.3
			Total 3350		Total 4.1
Darżlubie II- after colmatation	56.7	HF-CW I	1200	0.6	1.6
		Cascade filter	400		
		HF-CW II	500	0.6	0.5
		VF-CW	250	1.0	0.7
		HF-CW III	1000	0.6	1.3
			Total 3350		Total 4.1
Sobiechy*	7.6	HF-CW	448	0.6	2.1
		VF-CW	44	1.0	0.2
			Total 492		Total 2.3

*) The sewage outflowing from the VF-CW bed was recirculated

tank effluents in plant No. 5 was caused by the improper construction of the outflow of this tank that led to decomposition of sewage before the wetland system. The overall contaminant removal efficiency for local CW near Lublin ranged as follows: 55.1-97.6 %, 22.4-75.3 %, and 40-97 % for BOD_5, N_{tot}, and P_{tot}, respectively (see Table 4).

The average concentration of characteristic contaminants in effluent from the studied CWs and the corresponding maximum permissible concentrations are shown in Fig. 1. The results obtained indicated that concentrations of suspended solids (SS) met the required quality standard in all CWs. Plant No. 1 slightly exceeded the maximum permissible concentration of BOD_5 and twice almost exceeded those of N_{tot} and P_{tot} for discharge to a lake. Plant No. 6 exceeded the maximum permissible concentrations of organic matter, N_{tot}, and P_{tot}. Systems Nos. 2 and 3, inhabited by willow, fulfilled all criteria regarding required outflow quality. Facility No. 5 only exceeded the maximum permissible concentration of N_{tot} for discharge to a lake.

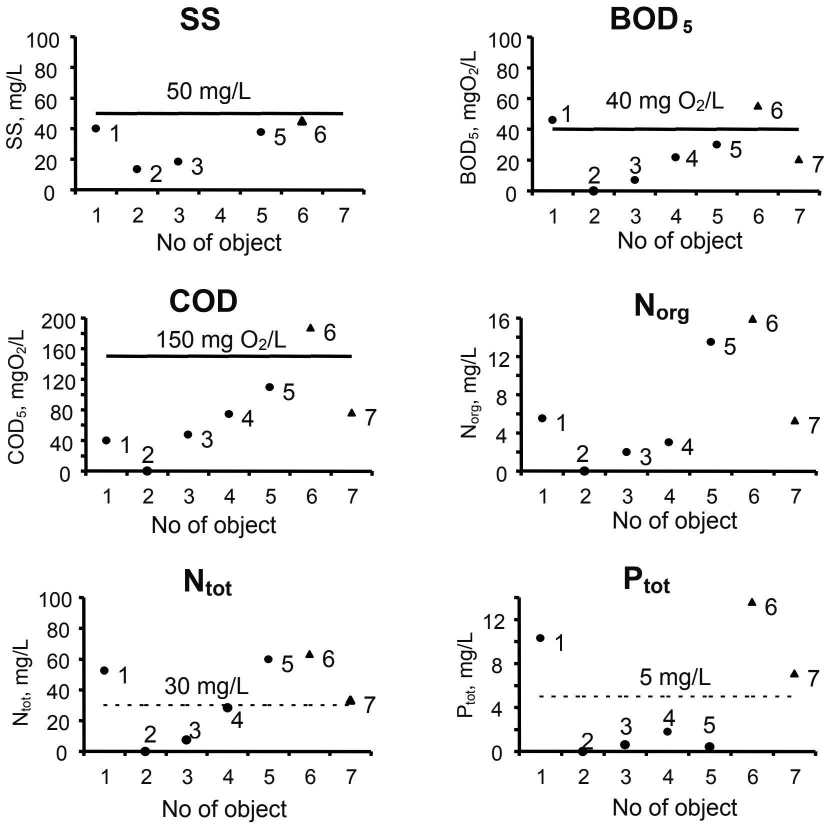


Figure 1. Average concentration of characteristic contaminants in effluents from analysed constructed wetlands: with willow (closed circles) and reeds (triangles) near Ostrołęki and near Lublin. Solid lines indicate maximum permissible levels of contaminants, whereas dotted lines correspond to maximum permissible levels in cases where sewage is discharged to lakes.

Improper operation of septic tanks and lack of a good link between subsequent units were the most frequent reasons of recontamination of sewage and lower efficiency of sewage treatment in the case of constructed wetlands Nos. 1, 6, 7, and partially for 4 and 5. Another reason for poor operation of plant No. 6 was its partial silting-up. These results indicated that all monitored constructed wetlands inhabited by willow (*Salix viminalis*) achieved a higher efficiency of phosphorus removal (over 80 %) compared to the plants inhabited with reeds (*Phragmites australis*). These suggest that the rhizosphere, i.e., the zone surrounding the roots of plants, of willow may create conditions for phosphorus removal, which does not take place in the case of the rhizosphere of reeds. Plants Nos. 5, 6, and 7, filled with subsoil, manifested lower efficiency of contamination removal than the plants filled with sorted material, which turned out to have better hydraulic conditions for sewage treatment (e.g., plants Nos. 2 and 3).

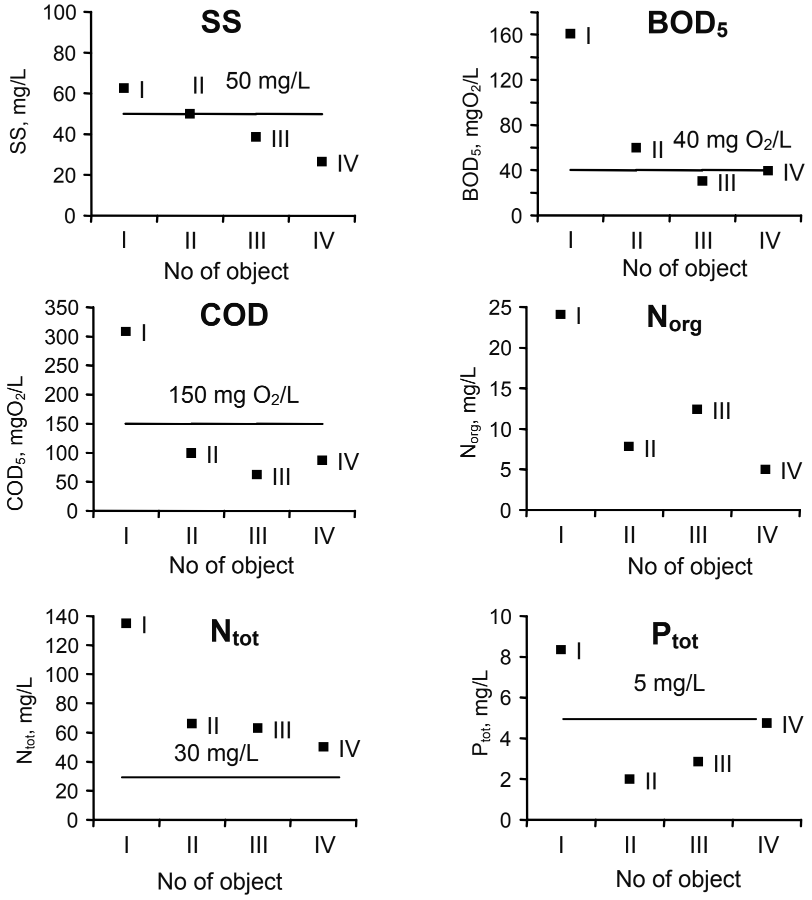


Figure 2. Average concentrations of characteristic contaminants in effluent from studied constructed wetlands near Ciechanów.

In the systems located near Ciechanow, there were no problems with operation of the septic tanks. In all plants, the septic tanks were of the same construction. Each tank was a circular concrete structure of total functional volume 9.6 m^3, divided into three equal chambers. The sewage retention time in the septic tanks depended on the number of inhabitants and ranged from 6.1 to 9.8 days. Pre-treated wastewater (i.e., septic tank effluent) was pumped out to the willow bed by a submersible pump located in the third chamber of the septic tank. In spite of high concentrations of contaminants in the inflowing sewage, the septic tanks worked properly. The beds were fed with wastewater periodically, usually 2 times a day. The volume of each dose was equal to 0.5

m^3 and the discharge time was only 5 min. Thus, the momentary loading rate was rather high. The average concentrations of the contaminants at the sewage outflowing from the willow beds located near Ciechanów are shown in Fig. 2.

The analysis showed that, in system I (the Antczak farm), purification of sewage was very poor. This was probably caused by the leakage around the vertical barrier in the bed, which resulted in shortening of the retention time (see Table 4). In system II (the Kuc farm), purification efficiency is also rather low. In this case, the reason is that the shape of the bed is a long rectangle (18 m × 1 m) and, at lower air temperatures, the wastewater cools quicker than in the "U"-shaped beds.

Table 4. Average removal efficiency of selected contaminants in individual farm's CWs.

System	Efficiency, %		
	BOD_5	N_{tot}	$N\text{-}NH_4^+$
1	79.8	50.8	-
2	99.1	22.4	-
3	87.6	75.3	-
4	55.1	61.7	-
5	80.2	47.9	-
6	97.6	47.7	-
7	91.6	46.9	-
I	24.5	39.9	41.5
II	79.3	84.2	86.4
III	75.4	69.7	70.3
IV	68.7	31.0	32.9
Wawrów (W)	66.8	38.5	43.9
Gralewo (G)	64.2	30.8	-
Małyszyn (M)	45.8	44.7	49.2
Rokotno (R)	78.7	24.2	37.0

Systems II, III and IV efficiently removed suspended solids and P_{tot}. Despite high efficiencies of BOD_5 (68.7-79.5 %) and N_{tot} removal (31.0-84.2 %), the concentrations of N_{tot} in the effluents were high due to high concentrations of $N\text{-}NH_4^+$ (47.8-57.5 mg/L) (Table 4).

The above result indicated that, in the investigated willow beds, sorption of NH_4^+ did not take place. This was due to using coarse-grained filling material and lack of conditions for nitrification in the beds with saturated subsurface horizontal flow. In the wastewater inflowing to and outflowing from the willow beds, no oxidised forms of nitrogen were found, indicating that ammonification is the dominant process in the beds.

The relationships between the mass loading rate and the mass removal rate of BOD_5 and N_{tot} are presented in Fig. 3. The removal rate of nitrogen in these systems changes widely between 2.1 and 22.7 kg/ha day.

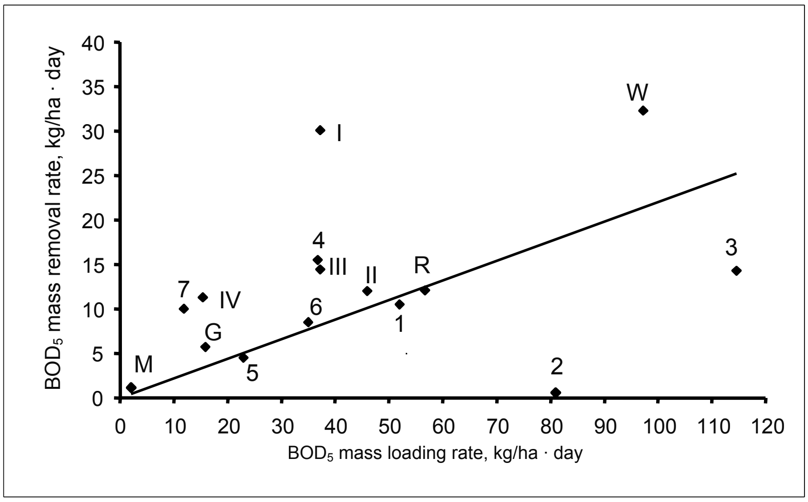


Figure 3a. Mass removal rate vs. mass loading rate for organic matter (BOD_5) in HF-CW household systems.

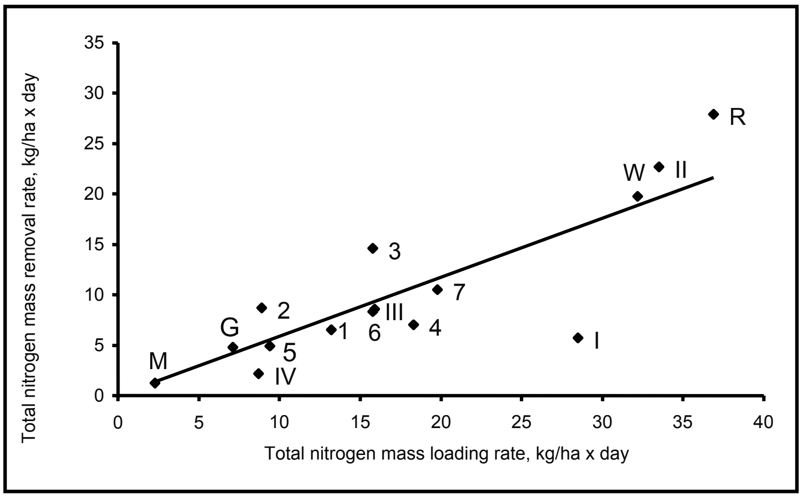


Figure 3b. Mass removal rate vs. mass loading rate for total nitrogen in HF-CW household systems.

Similar comparisons were carried out for four community HF-CWs located in Wawrów, Gralewo, Małyszyn, and Rokitno. Comparisons of organic matter (BOD_5), total nitrogen, ammonium nitrogen and total phosphorus concentrations in inflow and outflow of those systems are presented in Fig. 4. Only two systems with the lowest mass loading of organic matter (BOD_5) met the Polish outflow criteria; in one of the systems this parameter slightly exceeded the permissible value.

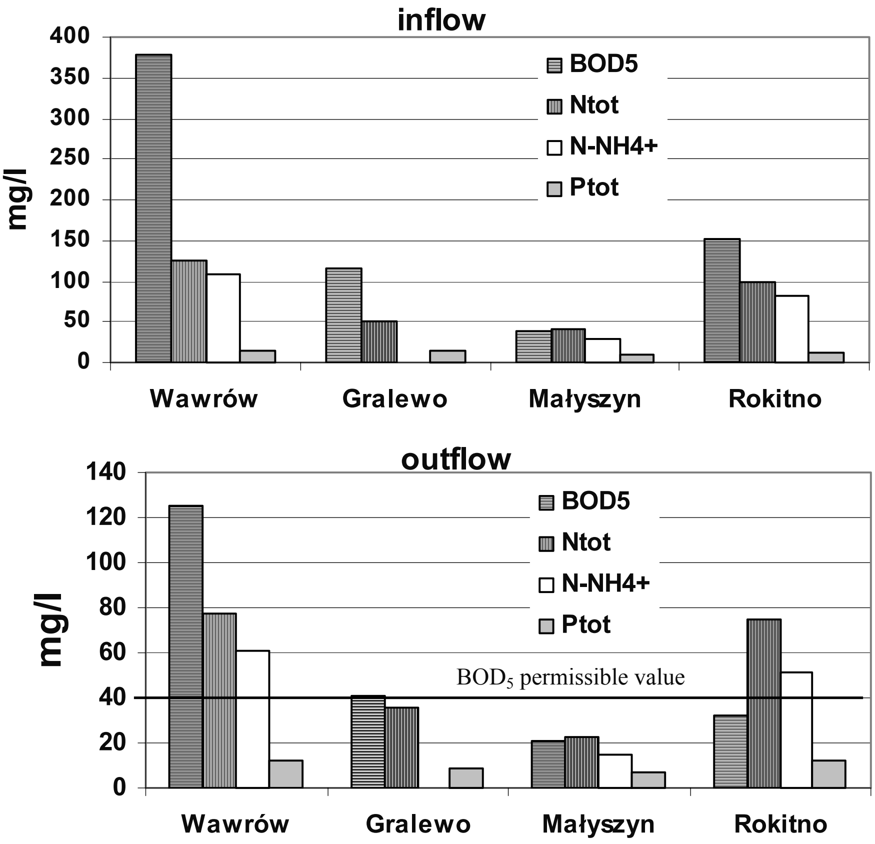


Figure 4. Average concentrations of selected contaminants in inflow and outflow in community HF-CWs located near Gorzów.

The loadings of total nitrogen and ammonia nitrogen (N-NH_4^+) varied widely from 2.3 to 36.9 and from 1.6 to 30.3, respectively. The efficiency of removal ranged from 56.5-75.6 % and 56.1-63.0 % for N_{tot} and N-NH_4^+, respectively. The relationships between the mass loading rate and the mass removal rate of BOD_5 and N_{tot} in these systems were presented above in Fig. 3a and 3b, respectively.

Hybrid Wetland Systems

The concentrations of organic matter (BOD_5) and nutrients in inflow and outflow of the hybrid systems are presented in Table 5. The facility in Darżlubie after colmatation did not meet the maximum permissible level for BOD_5 concentration, whereas the facility in Sarbsk only slightly exceeded this value. In general, decreasing the loading rate of nitrogen resulted in higher efficiency of its removal. In the case of Darżlubie and Sobiechy, operation of the VF-CWs was insufficient. Therefore, the concentration of total nitrogen in effluent exceeded the maximum permissible level.

Table 5. Concentration (mean ± SD) of organic matter (BOD$_5$), total nitrogen and total phosphorus in inflow and outflow in hybrid systems, mg/L.

System	BOD$_5$		N_{tot}		Pt_{ot}	
	inflow	outflow	inflow	outflow	inflow	outflow
Wiklino I- before modernisation	256.1 ± 22.3	27.2 ± 4.9	95.6 ± 11.8	19.7 ± 5.6	9.4 ± 1.3	3.0 ± 0.3
Wiklino II- after modernisation	273.0 ± 22.4	20.4 ± 6.8	88.8 ± 6.1	12.8. ± 0.5	10.1 ± 0.3	2.8 ± 0.2
Sarbsk	316.4 ± 98.2	42.0 ± 12.4	74.3 ± 13.0	16.7 ± 0.5	9.5 ± 1.9	3.9 ± 1.3
Darżlubie I- before colmatation	243.2 ± 34.1	20.1 ± 4.3	121 ± 21	37.1 ± 5.1	7.1 ± 2.3	15.5 ± 4.5
Darżlubie II- after colmatation	550.0 ± 124.1	204.5 ± 65.3	134 ± 10	48.1 ± 7.8	1.3 ± 0.4	4.7 ± 1.1
Sobiechy*	205.0	22.5	72.9	32.2	12.6	3.7

* from Ciupa (1996)

The efficiency of BOD$_5$ and total nitrogen removal in the hybrid constructed wetlands is presented in Fig. 5.

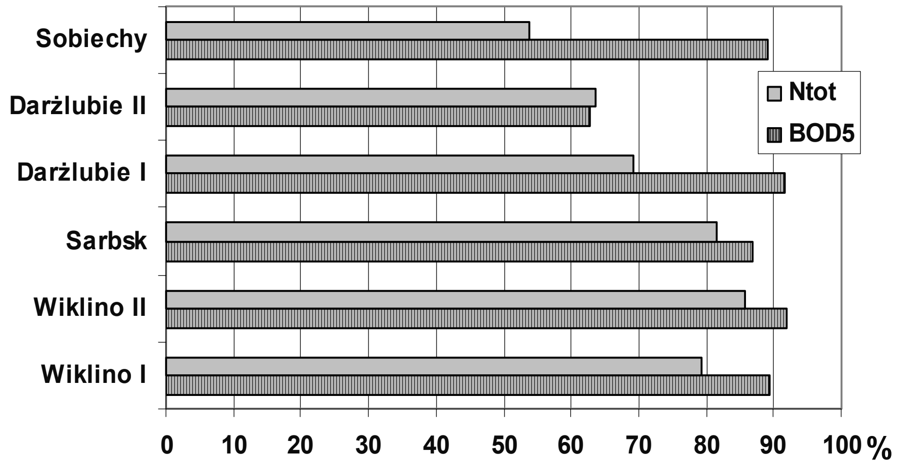
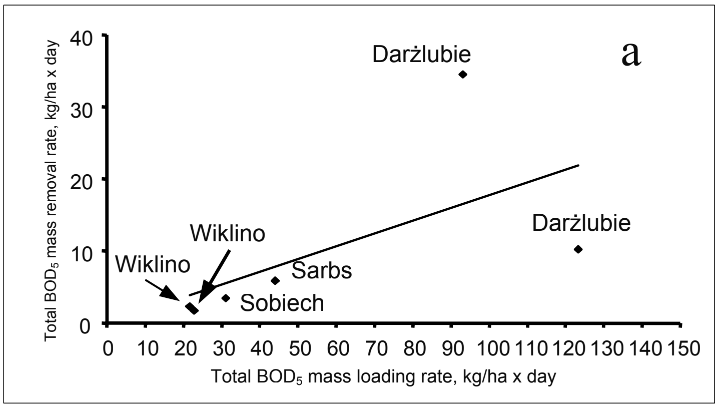


Figure 5. The efficiency of removal of organic matter and total nitrogen in hybrid constructed wetlands.

All systems analysed demonstrated a very high efficiency of BOD_5 removal, i.e., 90 % and more. The efficiency in Darżlubie II was lower (62.8 %) due to colmatation of the HF-CW I bed that caused a decrease of efficiency of removal in all CW facilities. In all hybrid CWs, the removal efficiency of total nitrogen was relatively stable and high (from 53.8 to 85.6 %).

The relationships between the mass removal rate and the mass loading rate of BOD_5 and N_{tot} are shown in Fig. 6. The average removal rate of BOD_5 was 7.8 kg/ha day. The removal rates of total nitrogen were more stable compared to one-stage systems and ranged from 4.2-14.6 kg/ha day. These values are very similar to values presented by Brix and Johansen (1999) (3.0-7.0 kg/ha day).



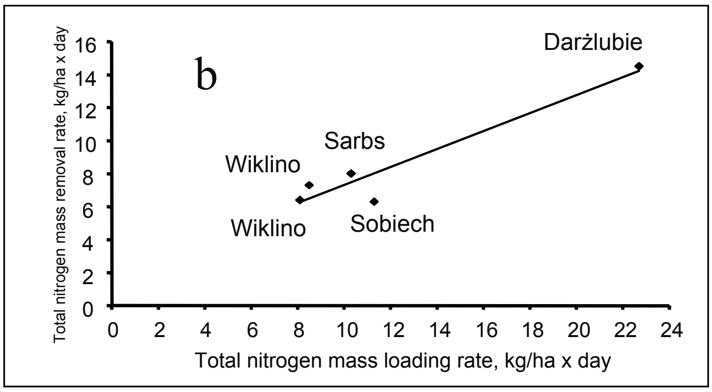


Figure 6. The relationships between the mass removal rate and the mass loading rate of BOD_5 (a) and N_{tot} (b) in hybrid systems.

Determination of average annual loads of nitrogen compounds enables estimation of the rate of ammonification, nitrification and denitrification processes in hybrid-constructed wetlands. Corresponding removal efficiencies were calculated as described in Methods. An example of such an estimate conducted for the Wiklino constructed wetland is shown in Table 6. The rate of denitrification was highest between three processes, probably, because part of the nitrate was transformed into free nitrogen due to denitrification. The ammonification process was the slowest. It was also demonstrated that, in the Wiklino constructed wetland, ammonification of organic nitrogen took place mainly during mechanical treatment (Gajewska and Obarska-Pempkowiak 2001).

Table 6. The rate of ammonification, nitrification and denitrification processes in subsequent stages of treatment in the Wiklino constructed wetland, g/m^2 day.

Processes	Stage of treatment			Total rate
	HF-CW I	VF-CW	HF-CW II	
Ammonification	0.15	0.15	0.13	0.15
Nitrification	0.68	0.53	0.35	0.56
Denitrificatin	0.67	0.59	0.51	0.59

Similar evaluations were carried out for constructed wetlands in Darżlubie. It was shown that the denitrification rate was equal to 0.98 g/m^2 day (Obarska-Pempkowiak 1999).

CONCLUSIONS

(i) Technological units for wastewater treatment consisting of septic tank and vegetated subsurface bed (willow or reeds) could be recommended for treatment of sewage in rural areas.
(ii) Faulty operation and maintenance of septic tanks, surface run-offs, and improper shape of beds are the reasons for the low efficiency found in individual pilot systems.
(iii) The majority of investigated household and community HF-CWs provide effective removal of suspended solids and organic matter expressed in terms of BOD$_5$.
(iv) A number of the investigated household and community HF-CWs did not provide effective removal of ammonia nitrogen due to the lack of conditions for nitrification and sorption.
(v) The hybrid constructed wetlands ensure high effectiveness of removal of organic matter and suspended solids enabling them to meet the new Polish requirements for effluents.
(vi) The hybrid constructed wetlands ensure a more stable removal rate of nitrogen compared to one-stage systems. The average removal rate in these systems was 7.8 kg/ha day.

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WATER AND PUBLIC HEALTH: LEGISLATION AS A TOOL FOR IMPROVING LIVING STANDARDS

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ABSTRACT

Limited capacity for renewal of ground and surface water and increasing demands from agriculture, industry and domestic users affect the quantity and quality of water resources. The links between the provision of clean water, sanitation and good health are so strong that protection and management of water becomes an indirect primary health protection issue. To prevent and overcome the variety of water-related health risks, implementation of various activities that include general environmental protection, development of water management systems, permanent water quality monitoring and control, and improvement of standards and legislature, are needed. Croatia has a long history of legislation that controls the quality of water. Both drinking water and surface waters are constantly monitored according to the existing laws and regulations. The legislation and implementation of various mechanisms of water protection as a tool for health protection are described.

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Modern Tools and Methods of Water Treatment for Improving Living Standards, 295–306.

WATER FOR HUMAN USE

Rapid industrial changes and increased pressure of people on ecosystems have caused global environmental changes that encompass global warming, stratospheric ozone depletion, resource depletion, loss of biodiversity, urbanization and widespread environmental pollution. Access to clean water has been taken for granted in most of the developed world, where water treatment technologies have eliminated most of the waterborne infections. On the other hand, polluted water, water shortage, and unsanitary living conditions kill 5 to 12 million people a year making "dirty water" the largest environmental killer around the world. It also prevents millions more from living healthy lives, and impairs the economic and developmental efforts of the country (Hinrichsen et al. 1998). About 2.3 billion people worldwide suffer from diseases that are linked to water, and most of the victims are children in developing countries (Hinrichsen et al. 1998, 2000). Safe drinking water would prevent around 2.5 million deaths from diarrheal diseases, 150 million cases of schistosomiasis or 75 million cases of trachoma each year (Hinrichsen et al. 1998, 2000).

At the same time, even the developed countries are facing new health threats in terms of limited water resources, increased salinity or transboundary pollution. Modern sensitive analytical methods, which are able to detect very low levels of contaminants, elevate the level of public awareness of a polluted environment. All this brings the safety of water supply into a new perspective, and environmental protection of water becomes an indirect primary health care activity. These are the reasons why United Nations and UNESCO declared the year 2003 the International Year of Water, and one of the objectives from the Kyoto Summit is to reduce the number of “thirsty” people by half by the year 2015.

Water-related diseases vary largely in their character, pathways of transmission, effects, and treatment. Traditionally, they were classified by the nature of pathogen, but such classification is not always useful for disease prevention. The more useful classification is based on different aspects of the environment, making the point for human intervention more recognisable. This classification puts diseases into five categories (Table 1) (WHO 2001).

In the region of southeast Europe, the most frequent water-borne diseases are transmitted by consumption of water contaminated by human, animal, and chemical waste. To prevent and overcome the variety of water-related health risks, implementation of various actions in both developed and developing countries is required. They include general environmental protection, development of water management systems, permanent water quality monitoring and control supported by adequate laboratory techniques, improvement of standards and legislature followed by enforcement of relevant laws. The means that secure the fulfilment of the above tasks should encompass technical, medical, ethical and economic aspects.

Table 1. Classification of diseases associated with water.

Disease category	Way of Transmission	Diseases	Incidence and risk	Prevention
Water-borne, Caused by both fecal-oral organisms and toxic substances	Consumption of water contaminated by human, animal or chemical waste	Cholera, typhoid, shigella, polio, meningitis, hepatitis A, diarrhea, cancer, neurological disorders, chronic diseases, low sperm count	Cause 12 million death per year, 4 billion cases of diarrhea per year; 1.2 billion people are at risk due to the lack of safe freshwater	Sanitary waste water disposal, water sanitation, industrial wastewaters treatment, agrochemicals use control
Water-dispersed	Aerogenic, through air-conditioners or showers	Respiratory diseases, Legionnaire's disease	Sporadic, unexpected, low risk	Sanitation of air and water distribution systems
Water-based	Aquatic organisms that spend part of their life cycles in water, and part in human/animal host	Dracunculiasis, paragonimiasis, clonorchiasis, schistosomiasis	Frequent in underdeveloped countries, deteriorate working ability and quality of life	Control of stagnant waters and number of transmitters, personal protection from contacts with transmitters, education
Water-related vector	Insects, mosquitoes, tsetse flies	Malaria, yellow fever, dengue fever, sleeping sickness, filariasis	Rising incidence, 2 billion people at risk of malaria alone	Control of insect’s breeding sites, personal protection, education
Water-scarce; develop where clean freshwater is scarce	Consumption of water polluted due to freshwater scarcity; poor sanitation due to the lack of water	Tuberculosis, tetanus, diphtheria, whooping cough, trachoma, leprosy	Spread in most of the world, the incidence is increasing	Improve water supply, better hygiene

WATER MANAGEMENT

Management in the field of water and water quality is tightly connected to the economic and social sustainability of the state. Traditionally, water management has been based on the "command and control" approach. It represents a system of laws, directives, standards, norms or codes that usually prescribe the way of behaviour in a "top down" manner. This approach is suitable for the big water projects and point sources of pollution, but it has certain restrictions when it comes to the control of diffuse sources, source abatement or cleaner production (Harremoes 2002, Harremoes et al. 2002). Therefore, new economic instruments have been developed in the form of taxes, levies or subsidies (Middleton and Saunders 1997). There is an ongoing debate on the privatisation of public waterworks and resources. Although the pricing is needed to lower the consumption and classify different users (such as industry or agriculture), there are strong warnings of the dangers that would accompany that process. However, in order to implement those rules, consensus or general acceptance by the community and consumers is needed. A consensual approach along with an ethical approach has been developing recently, supported by the extension of the ethical concept to mutual relations of humans, all animals, the whole environment, the earth and the universe (Harremoes 2002). Not long ago, the issues of environmental pollution were just outside of the moral community rules. Today, we know that an ethical approach in regulation is necessary for the long-term prospects. The only problem is that changes in ethics, behaviour or motivations are slow, while the driving forces and pressures on the environment are changing rapidly. Thus, "command and control" or "economic instruments" with short time constants are more appropriate for quick reaction.

Public Health Relevance

Here, we will limit our description to analysis of the most common method of water quality management, i.e., the "command and control" approach. It is based on the guidelines proposed by the World Health Organization (WHO) and adopted in most countries in the world.

The WHO guidelines for drinking water quality are primarily aimed at protection of public health by determining the number of pollutants as health risk factors. The guidelines are intended to be used as a basis for the development of national standards. If properly implemented, they will ensure the safety of drinking water supplies through elimination or reduction to a minimal concentration of constituents of water that are known as hazardous to health (or as a risk to health) (WHO 1993, 1996, 1997, 1998). It must be emphasized that the recommended guideline values are not mandatory. Their definition could take into consideration local or national environmental, economic, social, and other conditions.

In developing the guideline values for potentially hazardous chemicals a daily per capita consumption of 2 litres of water by a person weighing 60 kg was generally assumed (WHO 1996, 1997, Gleick 1996). It can be said that this assumption is overestimated to be on the safe side; nevertheless precaution is needed due to the different climatic factors and greater sensitivity of infants and children. There are two principal sources of information on the effects caused by exposure to chemicals that can be used in deriving guideline values. The first one originates from studies on human populations, and the second one, which is used more often, comes from toxicity studies on laboratory animals. Such studies could be biased owing to the relatively small number of animals used and the relatively high doses administrated.

Guideline values can be expressed as tolerable daily intake (TDI) and acceptable daily intake (ADI). The TDI is an estimate of the amount of a substance in food or drinking water expressed on a body weight basis that can be ingested daily over a lifetime without considerable health risk. ADIs are established for food additives and pesticide residues that occur in food due to necessary technological purposes or plant protection reasons, but in essence it has the same meaning as TDI. For chemical contaminants, which usually have no intended function in drinking water, the term “tolerable daily intake” is seen as more appropriate than “acceptable daily intake”, as it signifies permissibility rather than acceptability (WHO 1996, 1997).

Drinking water is usually not the only source of the exposure. In many cases, chemical intake from water could be small in comparison with other sources, but guidelines derived using the TDI approach take into account exposure from all sources and apportion a percentage of the TDI to drinking water. This approach ensures that the total daily intake from all sources does not exceed the TDI (WHO 1996, 1997).

Although WHO recommends parameters that should be monitored in drinking water, each country, in accordance with its own specific situation, needs and technical possibilities, decides how many of them will be implemented.

WATER QUALITY MANAGEMENT IN CROATIA

Croatia has a long history of legislation that controls the quality of water. The first written document that regulated protection and exploitation of water dates from the Kingdom of Croatia and Slavonia in 1891 (Šimunić 2001). In 1896, the city of Pula used hypochlorite in the typhoid epidemic (White 1972). That was the first recorded chlorine treatment of water in the world. Outbreaks of typhoid and dysentery, experiences from other countries, and development of cities lead to the adoption of water treatment by chlorinating in the late 19th and early 20th century in several cities (Dawson and Sartory 2000, Knowlton 2001). From that time, the larger cities chlorinated water sporadically, mostly when an epidemic would occur. The first relatively modern law for the territory of Croatia, which enforced mandatory chlorinating, dates from 1962. The same law regulated surface water protection as well, because developing industry started to discharge huge amounts of polluted water into sea, rivers, and lakes. This and all additional laws and regulations were formed to protect the physical, chemical, and biological characteristics of water by obligatory wastewater treatment and resource protection of drinking, mineral and thermal water. Today the laws are constantly being adjusted to the EU norms and regulations.

In Croatia, the Ministry of Health is responsible for the quality of drinking water, whereas the State Water Directorate has responsibility for all other water resources. Current legislation in the Republic of Croatia regulates all water categorization, quality standards, maximal allowed concentrations of toxic substances, water use, and protection. Based on measures for river body protection and on a number of parameters, three categories and five classes of surface water quality are defined in Croatia by the document "State Plan on Water Protection". Any surface water is officially categorized by the State Water Directorate (Official Gazette 1999), whereas a specific water class is assigned on the basis of real monitoring results (Official Gazette 1998).

The quality of drinking water is monitored by the Croatian National and County Institutes for Public Health and reported to the Ministry of Health. Control of drinking water quality in Croatia has a long tradition dating from 1931. According to the acting law, public water supply systems are constantly monitored. Local community water supply systems and private wells are being examined as well. However, from 1996, data reporting in the annual official publication has been discontinued and analyses have been performed sporadically and upon request. The quality of drinking water is assessed by analyzing various chemical, physical, and microbiological properties of water (parameters) prescribed by WHO and comparing the obtained results with standards. According to its needs, and technical possibilities, each country selects the most appropriate parameters to be monitored. Up to 1993, the number of required parameters for assessing the quality of drinking water in Croatia followed the increase of the number of parameters recommended by WHO, but afterwards the pace was lost (Fig. 1).

Today, fifty-eight parameters are determined and evaluated. Water Directorate and Croatian Waters for processing. Water quality monitoring

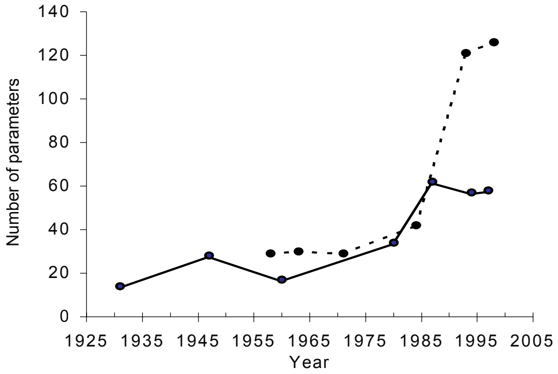

Figure 1. Dynamics of acceptance of required parameters for drinking water quality control in Croatia (solid line) in comparison with WHO recommendations (dotted line).

As far as surface waters are concerned, all rivers in Croatia are monitored by various state institutions and the data are reported to the State of the Danube catchment was established in 1963, and School of Public Health "A. Štampar" monitors the Drava River since that time. Initially, 14 parameters (suspended matter, dissolved oxygen, biological oxygen demand, chemical oxygen demand, pH, phenols, oils, most probable number of coliform bacteria, total number of bacteria, saprobic index, ammonium, nitrite, ortho-phosphate, and total dried residue) were examined. During the years, their number has increased (Fig. 2), but still did not reach the number of parameters prescribed by international conventions that Croatia has signed. To promote international collaboration and control of transboundary trafficking of contaminants, the Republic of Croatia signed a number of treaties, including the Bucharest Protocol 1985 (Protokol 1986). As an independent state, Croatia signed the Convention on the Protection and Use of Transboundary Watercourses and International Lakes in 1996 (agreed upon in Helsinki in 1992), and the Protocol on Water and Health in 1999 as part of it (Economic Commission 1992). Also Croatia signed Convention on Cooperation for the Protection and Sustainable Use of the Danube River in 1998 (agreed upon in 1994 in Sofia) (The International Commission 1994) and various bilateral agreements with neighboring countries Slovenia, Hungary, and Bosnia and Herzegovina.

The situation with both drinking and surface water are similar but only to some extent, because the WHO parameters (WHO 1993, 1997, 1998) are only recommendations, and each country decides how many of them it will implement considering its own specific situation and needs. For example, in Croatia, dioxins are not measured in drinking water. However, due to their

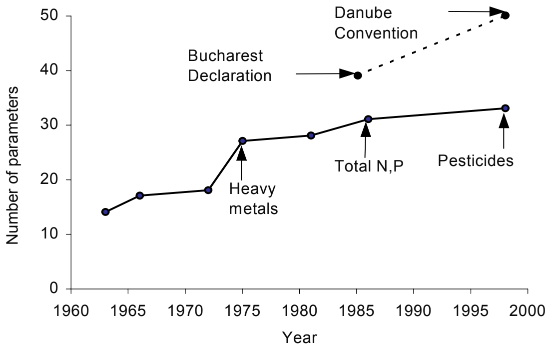

Figure 2. Dynamics of the increasing number of parameters for regular surface water monitoring in Croatia (solid line) in comparison with the requirements from international declarations (dotted line).

adverse health effect and fast formation, the dioxin concentration should be added to the obligatory parameters for evaluation of drinking water quality. The same request was posed (Puntarić et al. 2000) for the monitoring of foodstuff safety. Intensive use of pesticides, the synthesis of new types and their targeted use also calls for compound distinction in analysis. Regulations in Croatia define guideline values for combined pesticides and related compounds, which is not precise enough. We believe that this part of the regulations should adopt separate guideline values for each type of pesticide, as in many other countries.

In addition to the number of parameters, demands are put on analytical methods as well. It is of interest that up to the beginning of 1960s oils in water were determined only visually. The analytical methods have changed with time. At present, the Croatian methodology norms for examination of water and wastewater are based on American Public Health Association recommendations (Eaton et al. 1995), ISO, and EU norms (State Office 2000, 2001). Current trends in methodology are directed towards accelerating the analysis from the primary signal to the final result and to using the methods that are specific for a particular pollutant. The ability to selectively and efficiently screen for toxic compounds or pathogenic organisms improves water safety and, at the same time, protects the population in the case of natural disasters or chemical and biological warfare.

As mentioned above, public water supplies are constantly monitored, while local community water supplies as well as private wells are not under such rigorous control. Depending on the region and some other factors, monitoring of those facilities is organized and data shows that, from 1992 until 1996, out of 8000 samples more than 30% were chemically contaminated, whereas microbiological contamination was found in around

40%. Since 1996, there has been no mandatory monitoring of these water supplies. We strongly believe that during this time of biological and chemical warfare threat, as well as terrorist attacks, there is a need for quick reaction and alternative networks of water supplies. Knowledge on the status of local water supplies or private water wells and natural water springs could be crucial in such situations. The same could be considered in the case of natural disasters, especially earthquakes. The southern part of Croatia, Southern Dalmatia, could be taken as an example. It is located in the seismically active region with about 50 various movements of the earth yearly. Water supply is public, alternative water supplies are cisterns; they are scarce and abandoned, with no mapping, let alone monitoring of water springs or other water resources.

RECENT TRENDS

Permanent monitoring and data collection is important for understanding the changing environment, assessing emerging health needs and projecting possible long-term impacts. Laboratory expertise is required for the assessment, assurance, and policy making in each country. Sudden environmental changes may indicate a need to modify global strategies, existing policies or their development. Also, monitoring directly supports the local or state health departments in preserving and enhancing the health of the people and enforcing environmental laws. A monitoring and evaluation system is created to help keep the global picture in mind, while looking closely to specific issues. WHO has identified contaminants that are potentially hazardous to human health and along with microbiological organisms, the possible effects of 128 chemical contaminants can be assessed through comparison with guideline values (WHO 1993, 1997, 1998).

Since the number of parameters and the area of monitoring are extremely wide the actual data collection could be very expensive and administratively demanding, Croatia is moving towards the indicator system according to the European Environmental Agency (EEA) and Eurostat (Smeets and Weterings 1999, European Environmental Agency 2000). Given the complexity of issues of quantity and quality of waters, it is necessary to present those data in the forms that are recognizable for those who are managing water resources. The indicators are more efficient for the follow up of the various changes in the systems, strategies or sectorial goals, as well as for comparison of the data and standardization of reporting. In Croatia, the data collected were neither evaluated nor reported in accordance with requirements of the EU documents, except for some data concerning seawater quality. The indicator system is based on indicators of driving forces, pressures, state, impact and response (DPSIR) according EEA typology (Smeets and Weterings 1999). Indicator of driving forces describes basic mechanisms of the negative impact, for example, industry or agriculture; pressure describes the consequence of those mechanisms, while state represents present conditions, and impact is the consequence of the pressure. Response is the last indicator that comprises various acts, conventions or activities that prevent pressures. Today, we have developed 60 indicators, of which 20% are driving forces, 26% - pressures and 54% - state. Most of the indicators are for surface waters, and only 26% of them are available for application at present. Shortly, another 18% will be available, while for the remaining 56% additional data still needs to be obtained. There is an opinion that, beside the indicators representing EU water politics, certain national indicators should be developed to serve transitional processes.

The most important European Union document that determines the long-term water policy is the Water Framework Directive adopted in December 2000 (European Parliament 2000). The Directive establishes the framework of water policy through the implementation of principles of sustainable development and integral management of water resources. Although national legislation in Croatia in the water sector is basically in accordance with the basic principles of the Directive, certain expansion of the policy concerning extent and means of freshwater, sea and water ecosystems protection remains to be conducted. The Agreement on Stability Pact and Accession to the EU brings Croatia into the process of harmonisation of national legislation with that of the EU, which is particularly important for water management. This process is predicted to end by 2005.

CONCLUSIONS

So far, water management in Croatia is more supply oriented, but, for the future, the relevant question should be how can we best benefit by stopping living as if we have unlimited water resources. From the described data, it is evident that Croatia faces a lot of conceptual and technical demands. Constant harmonization of Croatian and EU laws, both in terms of guideline values and analytical methods, and pursuing the obligations implemented into signed international conventions represent permanent tasks. Conceptually, Croatia needs to follow new scientific and economic trends in water management, considering water as an economic category, the same as infrastructure, energy, or human knowledge supporting sustainable development. Awareness that environment and health, as well as sustainable development, are linked should constantly be kept alive. Generally speaking, while the cost of building freshwater supply systems and sanitation facilities is high, the costs of *not* doing so can become enormous. Another aspect is saving water in everyday use. The need for permanent education and mobilisation of the population in this respect should be emphasised. Unfortunately, few countries, whether developing or industrialized ones, have adequately safeguarded water consumption and controlled water pollution. Others pose a global public health problem by not having standards to control water pollution adequately or by not enforcing their application. Croatia is somewhere in between and efforts should be made to shift toward better water protection and management.

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THE NATIONAL PROGRAMME FOR CONSTRUCTION OF URBAN WASTEWATER TREATMENT PLANTS IN THE REPUBLIC OF BULGARIA

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ABSTRACT

Bulgaria is among the Central and East European countries applying for membership in the European Union. One of the priority objectives of the country is getting into compliance with the EU legislation within the shortest possible time. This paper is focused on water protection and water quality management. The description of the current status on the discharge and treatment of urban and industrial wastewater is based on information from the inventory of urban wastewater treatment plants (WWTP) and the sewage network prepared for implementation of the EU Directive 91/271/EEC concerning urban wastewater treatment. The total amount of wastewater discharged into water bodies is 878,555,000 m^3 per year. The population connected to the urban collection system is 66.8%. The public sewerage discharges treated in urban wastewater treatment plants are 76%. There are 61 operational WWTP in Bulgaria. Some of them are completed, and others need additional measures for extension, reconstruction and modernization, since they operate below their designed capacity. In 1999, the National Program for priority construction of urban WWTP for settlements with over 10,000 equivalent inhabitants in Bulgaria was developed. The objective of the programme is to establish the priorities for construction of urban WWTP for all populated areas in the country with over 10,000 equivalent inhabitants, as well as the national short-term priorities until the year 2006. In 2003, the Implementation Programme for Directive 91/271/EEC concerning urban wastewater treatment has been developed. Identification of "sensitive areas"

A. Omelchenko et al (eds.),
Modern Tools and Methods of Water Treatment for Improving Living Standards, 307–314.

was conducted for all rivers in Bulgaria. Criteria for the construction of collection systems and WWTP are presented.

INTRODUCTION

Bulgaria is a pre-accession country and one of the main objectives of the country is getting into compliance with the EU legislation within the shortest possible time. Among the most important directives, which are related to water protection and prevention, are the following:

(i) Regulation on the way and order of industrial wastewater discharge in the urban sewerage systems (Dir. 76/464/EEC; 91/271/EEC);

(ii) Regulation on the quality of the water intended for human consumption (Dir. 98/83/EEC);

(iii) Regulation on the quality requirements of surface water intended for drinking purposes (75/440/EEC);

(iv) Regulation on the prevention of nitrates pollution caused by agriculture (Dir. 91/676/EC);

(v) Regulation on the quality of bathing water (Dir. 76/160/EC);

Regulation on the quality of fish and shellfish water (Dir. 78/659/EEC and 79/923/EEC);

(vi) Regulation on the quality of coastal sea water (Dir. 79/923/EEC; 76/464/EEC; 91/271/EC and 76/160/EEC);

(vii) Regulation on the emission limit values of dangerous and hazardous substances in discharged wastewater (Dir. 76/464/EEC);

(viii) Regulation on the procedure and manner for establishment of networks and on the operation of the National Water Monitoring System;

(ix) Regulation on the research, use and prevention of the ground water (Dir. 80/68/EEC and 76/464/EEC);

(x) Regulation on the sanitary protected areas (Dir. 75/440/EEC; 80/68/EEC; 91/676/EEC);

(xi) Regulation on the wastewater discharge permits issue and individual emission limit values for point sources of pollution (Dir. 80/68/EEC; 76/464/EEC and 91/271/EC)

This paper is focused on the implementation of the EU legislation concerning water protection and water quality management.

IMPLEMENTATION OF THE EU LEGISLATION CONCERNING WATER PROTECTION AND WATER QUALITY MANAGEMENT[1]

The water protection process in Bulgaria started with assessment of the current situation; then continued with development of the National

Programme in accordance with the international commitment of the country and the EU legislation.

National Programme for Priority Construction of Urban Wastewater Treatment Plants for Populated Areas with Over 10,000 Equivalent Inhabitants in the Republic of Bulgaria

The National Programme (Ministry of Environment and Water 1999) was developed for priority construction of urban WWTP for settlements with over 10,000 equivalent inhabitants in Bulgaria. The objective of the programme was to establish the priorities for construction of WWTP for all urban areas in the country having a population of more than 10,000 equivalent inhabitants, including the national short-term priorities until the year 2006 defined for specific river basins. It was intended that the programme would be extended in the future, by developing adequate additions.

The reports on the implementation, which were sent to the EU, were based on the following data: the total amount of wastewater discharged into water bodies is 878,555,000 m^3 per year or 2,407,000 m^3 per day; the population connected to the urban collection system is 66.8%; 76 % of public sewage discharges are treated in urban WWTP; there are 61 operational WWTP in Bulgaria - some of them are fully-functional, and others need additional measures for extension, reconstruction and modernization, since they operate below their designed capacity.

Among the reasons for such low-efficient working were the following: (i) incomplete construction of the treatment plants (mainly related to the treatment of the sludge); (ii) weaknesses and errors during design; (iii) errors during construction; (iv) low level of automation during management and control of the processes; and (v) the absence of the necessary repair work for the installations.

The need for improvement necessitates the assessment of the priorities. The assessment of the priorities for construction, completion, extension, reconstruction or modernization of the WWTP for urban wastewater was made, using the following criteria:

1. Number of the population at health risk resulting from pollution of the water recipient body by municipal sewerage and industrial wastewaters. The most common situations for such pollution are: (i) discharging wastewaters in the immediate vicinity of the water intake installations, which provide water for municipal drinking water supply, and (ii) discharging wastewaters in the immediate vicinity of the beaches on the Black Sea coast and other sites, where the waters are used for bathing.
2. Emission status and category of the wastewater recipient body.
3. Location of the discharging point of untreated wastewaters: (i) in environmentally damaged zones where the water quality in the water recipient

body does not correspond to the designated category; (ii) in the upper course of the rivers; (iii) in the areas of protected territories or sensitive ecosystems.
4. Number of equivalent inhabitants of the populated areas, which defines the water quality to be treated by the WWTP.
5. The extent of completion and use of the existing sewer network and collector for the future treatment plant.
6. The extent of completion of the treatment plants under construction.
7. International commitments of the country.
8. Existence of a designated site for the urban WWTP, project readiness and decision on the environmental impact assessment report.
9. Necessary capital costs for the partial or complete realization of the project and comparison with expected environmental effects.
10. Allocated sources of financing for realization of the project and possibilities for partial external financing.
11. Commitment of the local authorities to realization of the project.
12. Clarification of the ownership of the water supply and sewer networks and installations.

The national programme for priority construction of urban WWTP was conducted in accordance with the main principles of the European legislation regarding water quality management. The programme created the necessary prerequisites for practical implementation of the European Directives, as well as the national short-term priorities until the year 2006.

Implementation Programme for Directive 91/271/EEC Concerning Urban Wastewater Treatment

The Implementation Programme (Ministry of Environment and Water 2003), together with additional information regarding the official Bulgarian position in the negotiations, was adopted by the Council of the Ministers on 4 April 2003. It is based on the previous developed programs and the needs of the country.

The objectives of the Implementation Programme are to prevent pollution of the inland surface and coastal waters by regulating the collection, treatment and discharge of wastewater from urban and industrial sources including discharge of biodegradable substances.

Directive 91/271/EEC sets a series of requirements with respect to the systems for collection, treatment and disposal of wastewater, and the related legal aspects and terms for implementation. For the needs of the implementation, an assessment of the current status was necessary. The assessment was conducted in the steps listed below:
(i) Legislation reflecting the requirements of the Directive 91/271/EC;
(ii) Competent bodies and responsibilities;

(iii) Procedure for issuing permits for discharging wastewater from the urban collection system;
(iv) Discharge and treatment of urban and industrial wastewater according to the Directive (Art. 13);
(v) Status of the national system for monitoring of surface and wastewaters; Identification of "sensitive areas" according to Annex 2 of the Directive;
(vi) Existing situation concerning the treatment of WWTP sludge.

The procedure for issuing permits for discharging wastewater from the urban collection system was adopted along with the Water Law in 1999 and the Regulation on Emission Standards[2] in 2000.

The distribution of the population living in settlements with WWTP at different stage of their construction is shown in Fig. 1.

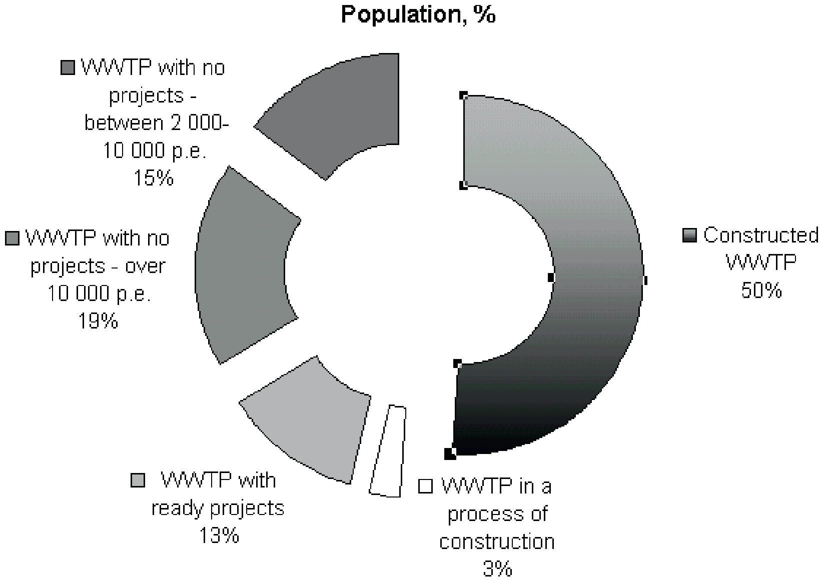

Figure 1. The distribution of the population living in settlements with WWTP depending on the stage of their construction.

The Ministry of Environment and Water (MOEW) is in charge of monitoring and reporting of the environmental state (quality) of the surface waters. This function is performed by the Executive Environmental Agency (EEA). The experts from Regional Inspectorates of the MOEW equipped with laboratories for water quality analyses periodically take water samples and carry out analysis. EEA represents a Bulgarian reporting center for the European Environmental Agency. It is also responsible for fulfilling the country's commitments for annual submission of reliable and updated environmental information to the European Environmental Agency.

Identification of "sensitive areas" was conducted for all rivers in Bulgaria. The study for identifying the “sensitive areas” for the rivers in South Bulgaria was implemented within a project BG – 9904-04.02 under the PHARE Program – Cross-Border Cooperation Bulgaria – Greece “Identification of the sensitive areas in the valleys of the rivers Mesta, Tundja, Struma, Arda and Maritsa in compliance with the criteria of the Directive 91/271/EC”. The project covered two of the four river basins in Bulgaria. The other river basins, the Danube and the Black Sea basins, were declared by Bulgaria to be sensitive areas.

After defining the necessary investments for each settlement to achieve the objectives of the Directive, the settlements were prioritized. The purpose was to distribute funds and efforts over the years according to the financial and technical capacity of the country.

Evaluation Criteria for Construction of Collection Networks and WWTP

The prioritization for the construction of collection systems is made on the basis of the following criteria (Ministry of Environment and Water 2003):
(i) Compliance with the requirements of Regulation No. 6 on the emission standards for admissible contents of harmful and dangerous substances in wastewater discharged into water bodies[2], based on the population equivalents in the settlements by groups, according to the requirements of Directive;
(ii) 91/271/EC concerning urban wastewater treatment;
(iii) Compliance with the requirements for construction of collection systems and urban wastewater treatment plants for settlements with population equivalent of more than 10,000 – by 1 January 2011;
(iv) Compliance with the requirements for construction of collection systems and urban wastewater treatment plants for settlements with population equivalent from 2,000 to 10,000 – by 1 January 2015;
(v) Wastewater from agglomerations of over 10,000 population equivalent entering the collection systems before being discharged into sensitive areas will be subject to the requirements under p. 2 and supplementary treatment for elimination of biogenic elements from the wastewater not later than 31 December 2010.
Wastewater from agglomerations of less than 2,000 population equivalent entering the collection systems before being discharged into surface fresh water and estuaries will be subject to appropriate treatment ensuring the water quality objective of the water body and observance of the Regulation No. 6 on the emission standards[2] not later than 31 December 2015.

Priority criteria for urban WWTP construction within the groups and conditions, set in p. I for each river valley in the country:

(1) Purpose and requirements of the wastewater receiving waters are identified:

(i) in sensitive areas, according to the criteria in Annex 4 to art. 12, item 1 of Regulation No. 6 on the emission standards[2] and Annex II to art. 5.1 of Directive 91/271/EC, concerning urban wastewater treatment;

(ii) in protected areas, according to the requirements of Regulation No. 4 for the quality of water for fish and shell-fish[3] and the Shellfish Water Directive 79/923/EEC and Freshwater Fish Directive 78/659/EEC and Directive 92/43/EC on the protection of natural habitats of wild flora and fauna;

(iii) in bathing waters, according to the requirements of Regulation No. 11 on the bathing water quality[4] and Bathing Water Directive 76/160/EC;

(iv) in regions of existing or future water use or in sanitary zones within the Black Sea water area, according to Regulation No. 8 on the quality of the coastal sea water[5].

(v) in sanitary zones, according to Regulation No. 3 on the conditions and terms for studying, designing, approving and operating sanitary zones[6].

(vi) in the upstream receiving water.

(2) International commitments of the country:

(i) Convention for cooperation for protection and sustainable use of the Danube River – ratified by the Republic of Bulgaria;

(ii) Convention for protecting the Black Sea from pollution – ratified by the Republic of Bulgaria;

(iii) Helsinki Convention for Protection and Use of Cross-border Rivers and International Lakes – to be ratified by the Republic of Bulgaria.

(3) Wastewater pollution load, risk for the human health and water quality objectives.

(4) The state of construction and use of the existing collection system and the collector to the location of the future treatment plant.

(5) The state of construction of the presently built treatment plants.

(6) Availability of a site for urban WWTP and a project for collection system construction.

(7) Necessary capital costs for the implementation of a stage or complete operation of the treatment plant and comparison with the expected ecological effect.

CONCLUSIONS

A strategy developed for implementation of the National Programme contains: (i) normative measures; (ii) administrative and organizational measures; (iii) financial measures; (iv) monitoring of the performance of the Implementation Program; and (v) Action Plan.

As a result of the analyses and the conclusions made on the situation in Bulgaria, it was concluded that meeting the requirements of the Directive could be threatened by the following main obstacles:
(i) extremely high investment costs needed for implementation;
(ii) long period of time nessessary for technological construction of the facilities of the water treatment plants.

A detailed plan for action was developed, which defines the responsible institution, deadlines, necessary funds, sources of funding, results and effects from the activity.

NOTES

[1] The information presented is based on description and analysis prepared for developing the implementation programme for the EU Directive 91/271/EEC concerning urban wastewater treatment and other requirements corresponding to the obligation for reporting to EC on the implementation process of the EU legislation in Bulgaria.

[2] Regulation No. 6 from 9 November 2000 on the emission standards for admissible contents of harmful and dangerous substances in wastewaters discharged into water bodies.

[3] Regulation No. 4 from 20 October 2002 on the requirements for the quality of water for fish and shellfish.

[4] Regulation No. 11 from 25 February 2002 on the bathing water quality.

[5] Regulation No 8 from 25 January 2001 on the quality of the coastal seawater.

[6] Regulation No 3 from 16 October 2001 on the conditions and terms for studying, projecting, approving and operating sanitary zones around the water sources and facilities for drinking water supply, or around mineral water sources used for medical needs and drinking.

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Ministry of Environment and Water 2003: Republic of Bulgaria, Implementation Programme for Directive 91/271/EC Concerning Urban Waste Water Treatment, report to the EC, adopted by the Council of the Ministers on 04 April 2003, Sofia, 2003.

WATER POLLUTION PREVENTION ACTIONS IN ROMANIAN INDUSTRY

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ABSTRACT

After more than 40 years of communist rule, Romania experienced a major regime change in 1989. Since it began its economic transition in 1990, Romania has taken a hesitant approach to reforms, and sought to protect vested interests and minimize the social costs associated with the transformation to a market economy. This strategy failed to produce sustainable gains in either economic or social conditions, and the costs have been higher than if a bolder approach to structural transformation had been adopted at the outset. Romania continued to face deepening economic recession, rising unemployment, and mounting problems stemming from lack of sufficient restructuring. In the first years of transition to a market economy, many industrial plants in Romania strongly diminished their production, this reduction ranging from 30 up to 80 %. The surviving plants will increase their production in the future. From an ecological point of view, the reduction of industrial production levels lead to a smaller number of pollution sources and smaller quantities of emitted pollutants. The transition period has represented, for the environment in Romania, a break in its fight with industrial pollution. This truce will be ended soon, and the only help for the environment will remain pollution prevention.

INTRODUCTION

The concept of life cycle assessment (LCA) is to evaluate the environmental effects associated with any given activity from the initial gathering of raw material from the earth until the point at which all residuals are returned to the earth. LCA is a technical tool to identify and evaluate

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opportunities to reduce the environmental effects associated with a specific product, production process, package, or activity. It can also be used to evaluate the effects of resource management options designed to create sustainable systems (Vignon et al. 1995). Implementation of opportunities pointed out in the third stage of LCA can be made by using pollution prevention techniques.

Pollution prevention techniques can be broken down into four major categories (Hunt 1990): inventory management (inventory control and material control), production process revision (operation and maintenance procedures, material change and process equipment modification), volume reduction (source segregation and concentration), and recovery (on-site and off-site recovery).

Handling waste as if it were a product will reduce waste and increase the potential for recovery. Allowing a recyclable or clean waste material to be contaminated may reduce or eliminate any recovery potential. This approach can be very cost - effective when the waste material is recoverable or has some market value (Mebratu 1998). Recovery of wastes can eliminate waste disposal costs, reduce raw material costs, and possibly provide income from a valuable waste. Significant amounts of waste can be reduced through improvements in the way a production process is operated and maintained. This approach is one of the most overlooked of all waste reduction areas because many wasteful operation practices have gone on so long they have become standard operating procedures (Freeman 1995). Improvements in operation and maintenance are usually relatively simple and cost-effective.

Installing more efficient process equipment or modifying existing equipment to take advantage of better production techniques may reduce waste generation. New or updated equipment can use process materials more efficiently, producing less waste.

METALLURGICAL INDUSTRY

Iron and steel manufacturing involves a series of complex processes whereby iron ore is converted into steel products using coke and limestone. The conversion processes comprise the following steps: coke production from coal and by-product recovery, ore preparation (sintering, pelletizing), iron production, steel production, casting, rolling and finishing. These steps may be integrated at one facility or completed separately at various locations. An alternative way to produce steel is by melting recycled scrap in an electric arc furnace and adjusting the chemical composition by adding alloying elements in a ladle furnace.

This chapter presents the results of a case study of LCA and some pollution prevention measures taken in one of the biggest Romanian iron and steel factory, SIDEX Galati (Harceag et al. 1999).

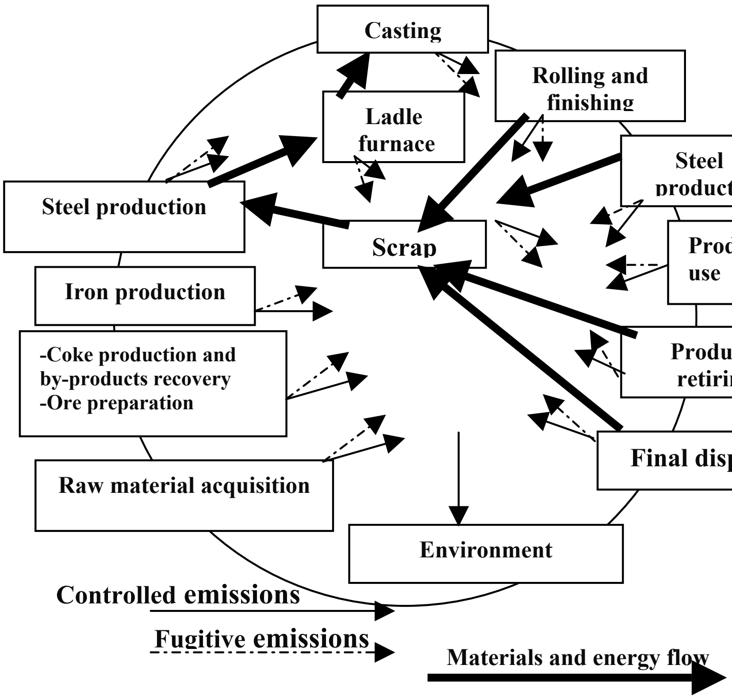

Figure 1. LCA scheme of the entire process of steel production.

Using LCA results and established pollution prevention measures (see Table 1), industrial managers have the opportunity to choose for industrial modernization such technologies so as to achieve maximum effect at the lowest cost. They are only low and non-waste technologies focused on source reduction or recycling activities, either requiring greater capital investment, or saving money in their operation, through more efficient use of valuable resources and reduced waste treatment and disposal costs. Installing more efficient process equipment or modifying existing equipment to take advantage of better production techniques may reduce waste generation. New or updated equipment can use process materials more efficiently, producing less waste.

AGRICULTURAL USE OF ANIMAL MANURE

Development of the zootechnic sector in Romania in the last decades was made, generally, without care regarding its environmental impact. This way animal manure, which can constitute nutritive resources for vegetable production, becomes a pollution source (Negulescu 1977).

Table 1. Pollution prevention measures.

Industrial activity	*Proposed measures*	*Results*
Raw materials storage	Moisten raw materials	Avoiding air pollution by wind
Ore preparation - sintering installation improvement	Advanced control of burning front: best distribution of coke granulation in the sintering bed; best gas permeability through the sintering bed (good preparation of raw materials); reduction of false air exhausting; modernization of ignition system (start burning at high temperatures).	Decreasing electricity consumption and consequently a decrease pollutant emissions
Ore preparation - sintering installation improvement	Increasing efficiency of heat use: reusing gas heat for preheating combustion air and raw materials; reusing the heat of sinter cooling air for preheating combustion air and raw materials; reduction of heat losses as a result of decreasing sinter returned material; re-circulation of sintering gases.	Decreasing electricity consumption and consequently a decreasepollutant emissions
Iron production	Removal of a part of coke with fine divided coal by injection in the blast furnace	Diminution of coke quantity production
Steel production	Steel-making process improvement (using oxygen, increasing process automation and control of emissions	Decreasing electricity consumption and pollutant emissions

Wastewater from industrial complexes for pig breeding results from washing platforms containing half-solid residuals (animal manure, straw and scraps). It contains large quantities of suspended solids, organic substances (expressed as COD and BOD_5), and inorganic nutritive substances with nitrogen and phosphorous (Negulescu 1987). It has to be treated by mechanical, biological and, many times, advanced means before discharge into a surface receiving water (Fig. 2). In Romania only about 15 % of the existing wastewater treatment plant for pig complexes are now in normal conditions of operation, 65 % of them are working improperly and about 18 % were never operational. Because of its composition, wastewater is useful for fertilizing agricultural land. Utilization of wastewater from pig complexes to irrigate agricultural lands is profitable for two reasons: to recover water necessary for agricultural cultures and also nutritive substances in wastewater and to avoid wastewater with potential pollution potential to discharge into a receiving water. The time for manure/wastewater/fermented sludge spreading on the arable land has to be carefully selected to suit local and geo-climatic conditions, and also agricultural culture type. The parameters that have to be

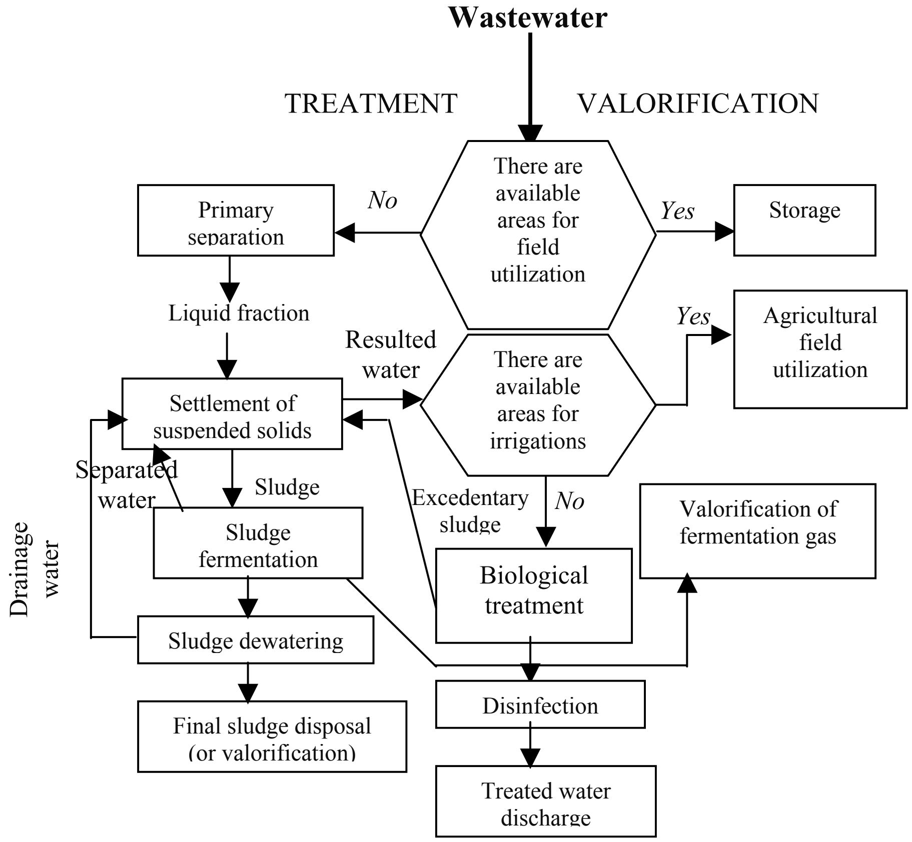

Figure 2. Wastewater from pig breeding treatment/valorification.

taken into account for manure spreading system design are: soil types, land slope,drainage capacity of soil and maximum quantity of residuals which can be used. Accumulated experience in animal manure agricultural use show that the quantity used in one year must to not exceed an equivalent of 250 kg of total nitrogen on one hectare.

Animal manure (wastewater and/or fermented sludge) can be used instead of artificial fertilisers only if there are available agricultural lands. If not, residuals have to be treated before discharging in order to comply with required norms.

OIL STORAGE AT OIL TERMINAL CONSTANTA

The oil terminal complex at the port of Constanta on the Black Sea is a major component of Romania’s oil industry infrastructure. The terminal is operated by SC Oil Terminal SA, a company founded in 1898 and presently responsible for the second largest oil terminal complex in Europe. It handles the import and the export of crude oil, refined oil products, petrochemicals and chemical products. It is designed to handle 24 million tones of imported crude oil and 10 million tones of exports each year. For a variety of reasons, the terminal is currently operating well below its design capacity. The Oil Terminal Constanta has three Tank Farms: North Terminal, South Terminal and Port Terminal.

A team formed by British and Romanian consultants performed a project funded by the EC PHARE Programme in the field of oil storage, "Assistance in the Preparation of the Privatization of the Constanta Oil Terminal". The project has been designed to deal with the most urgent environmental issues at the facility in order to control on-going pollution, particularly to ground water. It can be noted that the majority of environmental actions, established to determine the investments required to achieve Operating Permits and Operational Compliance are pollution prevention actions. Identified key prioritization issues included:

(i) Oil Terminal Development Strategy: The investment programme must take into account how the oil terminal is likely to develop in the future. It is our understanding that in the short to medium term, the oil terminal is likely to expand the South Terminal Tank Farm, with the North Terminal Tank Farms 1 and 2 becoming redundant. Given that the North Terminal Tank Farms are surrounded by municipal areas there is pressure to vacate the sites and make them available for municipal-type development. It is forecast that the North Terminal Tank Farm 2 will shortly be decommissioned, whilst the North Terminal Tank Farm 1 may remain in use for the next 10 years. Given that the North Terminal Tank Farms are unlikely to be included in the Oil Terminal's long-term development plan, equipment/plant investment may need to focus on the Port Terminal and the South Terminal Tank Farm.

(ii) Control of Product Pollution Sources: It is apparent that there have been a number of historical pollution incidents at the site and ground and groundwater contamination with petroleum products is ongoing. Whilst occurrence of environmental contamination is an environmental liability, the emphasis for this Project is pollution product source control. Environmental pollution is occurring generally due to problems associated with degraded and inadequate equipment and some pollution sources are due to operational practices.

(iii) Severity of Environmental Impact: priority will be given to targeting where indicated environmental impacts are of greatest concern. This is of particular relevance to identified environmental liabilities and their potential effect on terminal privatization/expansion.

(iv) Environmental Pollution Prevention: priority may need to be given to actions that are required to prevent future environmental pollution problems.

This refers to oil spillage containment activities, as well as marine spillage incidents.

(v) Waste Management Practices: priority may need to be given to actions that are required to prevent future environmental pollution problems caused by existing waste management operations.

(vi) Investment Costs: actions can be prioritized if there is value for money. This refers to where a relatively small financial investment has a proportionally large environmental benefit.

(vii) Length of Time to Implement: priority will be given to actions that can be implemented within the programme of this Project.

(viii) Definition of Party Responsibilities: from consultations with the Port Authority, it is clear that the responsibilities of the oil terminal with respect to marine oil spillages are limited – this will be taken into account when defining requirements for any marine oil spill control equipment.

(ix) Applicable Laws and Regulations: applicable funds will be targeted so as to assist the Oil Terminal Constanta to achieve environmental compliance. It is noted that compliance with certain environmental criteria is required in order for the terminal to obtain operational permits and as such is critically important.

The Study Team has identified a "long list" of required improvement works, these need to be taken through a prioritization task taking into account the issues as detailed above. The investments required to achieve Operating Permits and Operational Compliance are divided between South and Port Terminal, because the North Terminal is located in a residential area and its activities are to be restricted and undertaken by South and Port Terminals. The following investments were planned using the available 5.15 million Euro, mainly pollution prevention actions:

South Terminal

(i) Tank refurbishment of up to 16 tanks;
(ii) Excavate and dispose of waste oil in pit;
(iii) Repair of rail car loading area drainage system with provision of new loading hoses and ball valves;
(iv) Test and replace as necessary buried pipes;
(v) Install system along eastern boundary to intercept;
(vi) Off-site migration of oil products.

Port Terminal

(i) Waste water treatment system improvement;
(ii) Provision of new loading hoses and ball valves for rail car loading area;
(iii) Oil spill contingency equipment;
(iv) Replace the existing buried pipes with new;
(v) Above - ground pipes (from Port to South Terminal).

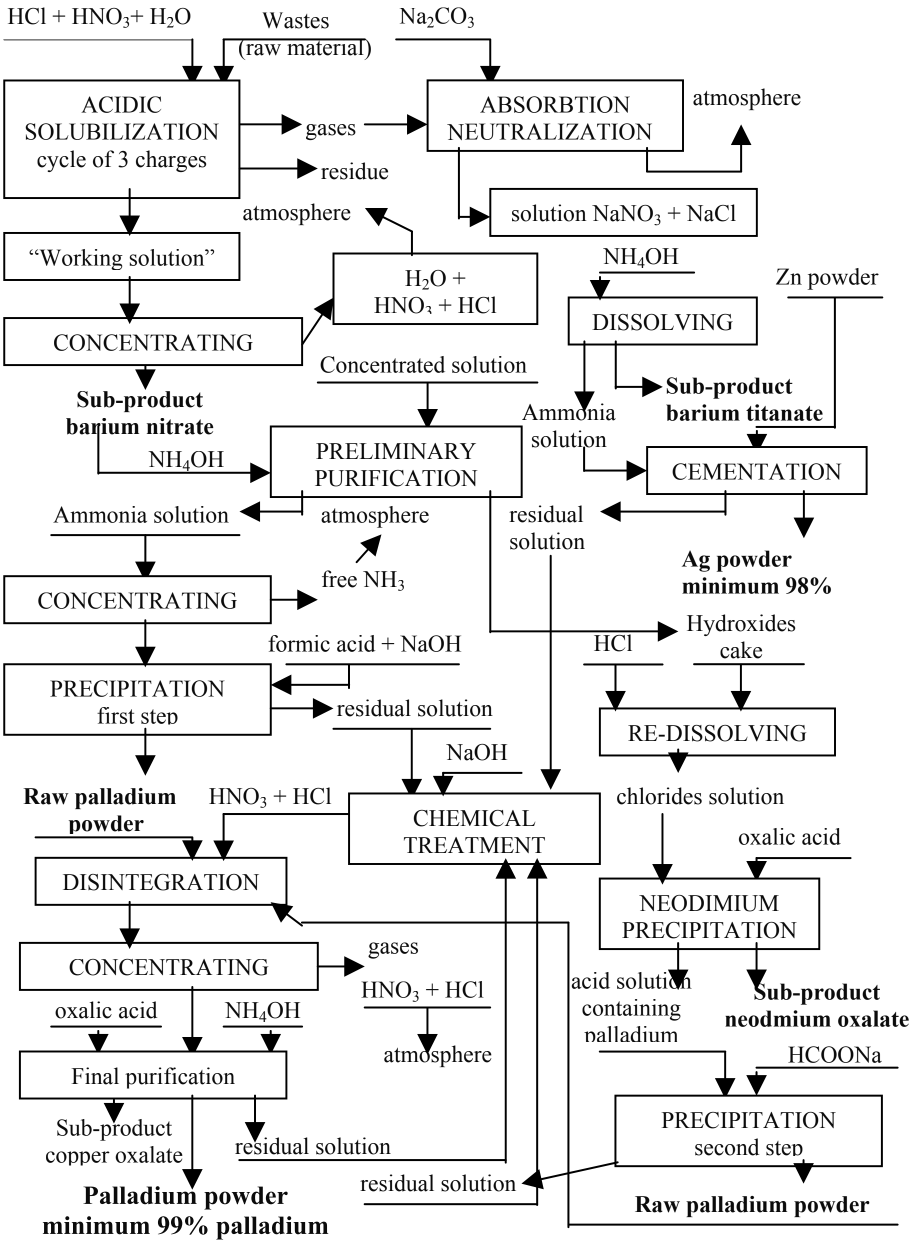

Figure 3. Technological scheme for palladium powder recovery from wastes.

USING WASTE AS RAW MATERIAL FOR RARE METALS RECOVERY

This section presents a chemical technology for rare metals (palladium, silver, and neodymium) recovery from wastes (generally ceramic wastes). It is a complex, unitary technology to treat wastes, which contain low quantities of palladium (1 to 4.5 %) and silver (1 to 4 %). It was developed for normal chemical and hydro-metallurgical working conditions: (i) acidic or alkali and/or ammonia dissolving; (ii) separation and purification through hydrolytic precipitation, siphoning and filtration; (iii) reduction in liquid medium, concentrations, etc.

Technological operations are made in glass and ceramic vessels, at normal pressure, at temperatures ranging between room temperature and the boiling temperature of the different systems. Washing water is recycled for increasing extraction and solution enrichment in metallic ions, and also for volume reduction of processed solutions. Products and co-products obtained are: metallic powder of palladium, silver, barium titanate, and neodymium oxalate. Wastes products are: ammonia, wastewater containing metallic ions, and remaining smaller quantities of solid waste. This technology is presented in Fig. 3.

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SURFACE LIPID COMPOSITION OF TWO EMERGENT WATER PLANTS USED IN CONSTRUCTED WETLANDS

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ABSTRACT

The emergent water plants *Juncus effusus* and *Typha latifolia* are studied as phytoremediants in constructed wetlands. Degradation of some toxic organic pollutants in the rhizosphere of plants may be followed by biochemical shifts in the surface lipids formation and change in their functions. The total fatty acid composition of surface lipids of these species was studied. An unusual composition of fatty acids and typical heavy isotopic discrimination for C_3-plants have been detected. The possible role of some lipid components in the protective functions of plant organism is discussed.

INTRODUCTION

Emergent water plants (helophytes) gain increasing application for wastewater treatment in constructed wetlands (Stottmeister et al. 2003). It was proved that traces of some volatile compounds, e.g., trichloroethylene, are transported unchanged from the rhizosphere to the phyllosphere via helophytes (Baeder-Bederski-Anteda 2002). Studies on the decontamination of air from volatile organic pollutants by plants were conducted by Cornejo et al. (1999). Nevertheless, the role of the plant surface lipids in such phytovolatilization and the reverse uptake of volatile compounds from the phyllosphere by plants is still not well understood.

It is suggested that the plant surface lipids play a significant role in the above-mentioned processes. Surface lipids (SL) form a layer of lipid molecules (e.g., epicuticular lipids and surface waxes) on the plant surface. Their main functions are to protect plants from UV-irradiation and to form a barrier for hydrophobic pollutants (Kunst et al. 2003). SL of plants are

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presently investigated in connection with the systematics of plants (Barthlott et al. 1998) and their occurence in fossils (Otto et al. 2001).

Substances originating from SL of plants constitute the main hydrocarbon components in atmospheric dust and, since C_3- and C_4-plants have different ability to discriminate heavy isotopes, the isotopic pattern of atmospheric hydrocarbons may provide hints regarding their origin (Conte et al. 2002). Some areas of biochemistry and physiology of SL remain enigmatic, especially transport of SL out of the cell and their participation in the processes of plant adaptation to contaminants.

Emergent water plants represent a branch of terrestrial plants, which evolutionally returned to water and developed a unique system of living in a mainly anoxic rhizosphere. SL of these plants might have a unique composition, as they must protect the photosynthetic system and other vital components of the plant cell against intensive sun radiation reflected from the water surface. Due to insufficient knowledge about the surface lipids of emergent water plants, we investigated the nature of the surface lipids of two emergent water plants broadly used in constructed wetlands for wastewater treatment.

METHODS

The plants *Typha latipholia L.* and *Juncus effusus L.* were grown in half-strength Hoagland solution prepared with tap water. The leaves of adult plants were collected and carefully extracted using boiling $CHCl_3$ to avoid extraction of cellular lipids. The extracts were collected, dried, saponified, reextracted and the total fraction of fatty acids (FA) of SL was collected as described in (Shtemenko et al. 1997).

FA were analysed as trimethylsilyl ethers (Tulloch 1984) by a gas chromatography-mass spectrometry (GC-MS) method using a gas chromatograph (HP 6890 Hewlet-Packard, USA) coupled to a mass spectrometer (HP 5973 Hewlet-Packard, USA). The GC was equipped with a capillary column (19091S-433, 30 mm×0.25 mm×0.25 μm film thickness, J&W Scientific, USA). The carrier gas was He. The oven temperature was initially set at 35 °C and held for 2 min. The temperature was then increased to 300 °C at a rate of 5°C/min and was held for 1 min. The GC was operated in a splitless mode with a purge time of 0.16 min, purge flow of 20 ml/min, and the injection port temperature kept at 180°C. The mass spectrometer was operated in the SIM mode.

The carbon isotope composition was measured with a GC-C-IRMS (gas chromatography/combustion/isotope - ratio - monitoring mass spectrometry) system (FINNIGAN MAT-252, Bremen, Germany) with the same chromatographic conditions as for GC-MS analysis. The isotopic composition of individual compounds was calculated by integration of the mass 44, 45 and 46 ion currents. Analyses were done in duplicate or triplicate with standard deviations (± 1 σ) better than 0.5%. The $\delta^{13}C$ values are expressed vs. Vienna Pee Dee belemnite (Richnow et al. 2003).

RESULTS AND DISCUSSION

The FA composition of the SL of the investigated plants is presented in Table 1.

Table 1. Fatty acid composition of SL of water plants, %.

Fatty acid	*Typha latifolia* L.	*Juncus effusus* L.
$C_{12:0}$	1.93	1.51
$C_{14:0}$	9.05	7.8
$C_{15:0}$	4.03	6.07
$C_{16:1}$	12.02	18.1
$C_{16:0}$	27.2	31.4
$C_{17:0}$	1.14	1.63
$C_{18:2}$	1.8	2.13
$C_{18:1}$	11.66	14.6
$C_{18:0}$	11.79	14.7
$C_{20:0}$	2.35	3.4
$C_{24:0}$	6.69	5.31
$C_{28:0}$	7.36	6.33
$C_{30:0}$	8.02	12.52

It can be seen that both the C_{16}- and C_{18}-fractions represent dominating FA of SL. Also, surprisingly, the large fraction (25 – 30%) of unsaturated FA, which is mainly due to large quantities of 9-*cis*-hexadecenoate ($C_{16:1}$), which has been detected. Both the above facts manifest an unusual composition of FA fractions of the investigated plants. In a comprehensive review (Bianchi 1995), the FA composition of SL was shown to be highly species-dependent. However, the common feature of SL of most plants is the domination of saturated long chain FA. In general, there is a lack of studies on FA composition of SL of various species, whereas composition of hydrocarbons, which were proposed as chemotaxonomic substances (Del Castillo et al. 1966), has been investigated more extensively. Many authors noticed the presence of unsaturated FA in SL but the role of double bonds in the SL components was not discussed at all. In our previous works, we showed that SL of grain of ordinary and mutant (Opaque-2) forms of maize differed very much in terms of quantities of unsaturated FA. We have found that the greater ability of mutants to contact with pests and the lower potential of adaptation to some environmental factors than that of the ordinary forms correlated with the lower content of unsaturated FA ($C_{18:1}$ + $C_{18:2}$) (Shtemenko et al. 1992). According to these investigations and taking into account the diversity and specific ways of SL formation in plants, it can be suggested that the water plants investigated have a specific biosynthetic mode of SL formation. It includes desaturating pathways that occur during formation of a surface layer closer to cellular membranes.

The stable carbon isotope compositions of all FA range from 25 to 33 % $\delta^{13}C$ and show typical heavy isotope discrimination for C_3-plants. The odd-numbered FA become relatively more depleted in ^{13}C with increasing chain-length. A similar feature was also found for alkanes (Schefuss et al. 2003). These facts do not have any explanation at present and require a special investigation.

Some unusual acids were found in the investigated plants (Table 2).

Table 2. Content of some unusual acids in SL of water plants, % of the fraction.

Acid	*Typha latifolia* L.	*Juncus effusus* L.
Anteisopentadecanoate	5.76	7.51
Cycloheptadecanoate	7.54	1.15
Dehydroabietic acid	5.51	1.07
Cyclopropanenonanoic acid	18.28	17.66

From our knowledge, cycloheptadecanoate and cyclopropanenonanoic acid with cyclic fragments were not found among biomolecules and their existence in SL in such essential quantities requires additional investigations. As for anteisopentadecanoate (3-methylpentadecanoate), the presence of this substance is not surprising since iso-(2-methyl)- and anteiso-(3-methyl)-chains, both odd and even, were previously found among branched alkanes in SL (Bianchi 1995). Also it is well known that FA are precursors of alkanes (Kunst et al. 2003). Branched chains usually occur in very small quantities among lipid components (under 2%) and their essential quantities in SL of the investigated water plants underline the specific mode of their biosynthesis. The structure of dehydroabietic acid is presented in Fig. 1.

This substance belongs to the family of diterpenes. The diterpene acids containing the abietane and pimarane skeletons were identified in SL of Pinacea (Pine tree family) and in tobacco leaves and seem to determine the resistance of the plant to insect attack (Bianchi 1995). The identification of dehydroabietic acid in the total FA fraction highlights the large quantities of this terpenoid acid in SL of these samples. Indeed, such substances are usually identified by column chromatography of the whole SL fraction and not by hydrolysis and re-extraction procedures. It is noteworthy that the tricyclic diterpenoids with and without double bonds in the non-aromatic rings are widely spread in the plant world (Otto et al. 2003). Their functions as

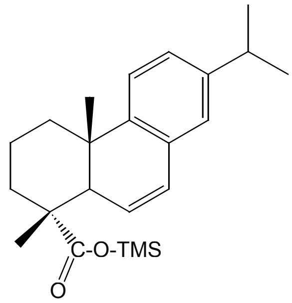

Figure1. Abieta-6, 8,11,13-tetranoic acid (trimethylsilylester derivative).

fungicides and pesticides are well recognized. Little is known about their role in formation of SL. According to the data obtained, it could be hypothesized that the investigated emergent water plants might have an additional protective mechanism against pests, as they live in humid conditions, through the synthesis of essential quantities of terpenoids in the surface layer.

CONCLUSIONS

Analysis of the results lead to the following conclusions. The fatty acid fraction of the emergent water plants *Typha latipholia L.,* and *Juncus effusus L.* has an unusual composition as compared to previously investigated plants. It relates to the molecular structure of the dominating substances, unsaturation of fatty acids, and the presence of cyclic and terpenoid compounds. The application of water plants for phytoremediation must be followed by investigations of surface lipids content, since many of the components may be involved in the biochemical processes of degradation of water pollutants.

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