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CINCINNATI, OH 45268

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FOREWORD

Today's rapidly developing technologies and industrial practices frequently carry with them the increased generation of materials, that if improperly dealt with, can threaten both public health and the environment. The U. S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of EPA with respect to drinking water, wastewater, pollution prevention, solid and hazardous waste, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between researchers and users.

These Abstract Proceedings from the 1994 Symposium provide the results of projects recently completed by RREL and current information on projects presently underway. Those wishing additional information on these projects are urged to contact the author or the EPA Project Officer.

RREL sponsors a symposium each year in order to assure that the results of its research efforts are rapidly transmitted to the user community.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

NOTICE

The abstracts presented in these Proceedings (with the exception of those from the Hazardous Substance Research Centers) have been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

The Twentieth Annual Risk Reduction Engineering Laboratory (RREL) Research Symposium was held in Cincinnati, Ohio, March 15-17, 1994. The purpose of this Symposium was to present the latest significant research findings from ongoing and recently completed projects funded by the Risk Reduction Engineering Laboratory.

These Proceedings are organized into two sections. Part One contains extended abstracts of the paper presentations. Part Two contains abstracts of the poster displays. Subjects include pollution prevention demonstrations and life cycle analysis; remediation technologies from the SITE Program, RREL technologies, and oil spills remediation technologies; drinking water and wastewater technologies; municipal solid waste technologies; and hazardous waste technologies.

ACKNOWLEDGEMENTS

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USING LIFE-CYCLE ASSESSMENT TO EVALUATE POLLUTION PREVENTION OPTIONS IN THE PRINTING INDUSTRY

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INTRODUCTION

The Risk Reduction Engineering Laboratory is evaluating the use of the Life-Cycle Assessment (LCA) approach in selecting pollution prevention (P^2) options. Typically, P^2 options which are available to a process operator for "improving" the process are assessed using limited information with the final selection often largely based on cost. The idea behind this study was to expand this decision-making process to include life-cycle, cradle-to-grave considerations leading to a better decision. A framework method was developed for calculating a matrix scoring system. A general framework was developed that can be applied to many different industries, however, only a subset of these criteria would be selected for evaluating P^2 activities for a specific industry. The lithographic printing industry was selected as a case study for illustrating the application of the framework.

METHODOLOGY

The preliminary framework methodology has been developed so that it can use industry average data for an entire industry or site-specific data for an individual company to determine which P^2 activities result in the greatest environmental improvement. This information can be used along with other factors, such as cost, manufacturability, and performance, to break a tie between similar P^2 activities. It is expected that users of this methodology include both industry and government.

The P^2/LCA methodology has some limitations. The alternatives are expressed in the form of fractions, where the denominator is the score for a criterion before application of a specific P^2 activity and the numerator is the score for the same criterion after implementation of that P^2 activity. A specific P^2 activity in a given industry can be compared on a relative basis with others calculated for the same industry to see which activity provides the greatest, relative to the original process, environmental improvement. However, the final result should not be used to claim that the process is good or bad for the environment. The "scores" are only for selected criteria in specific life-cycle stages that are expected to change due to the P^2 activity. The results are not based on all possible activities and do not represent all possible impacts in all life-cycle stages, and thus do not represent a full LCA.

A master list of impact categories was developed based on the work by SETAC. As defined by SETAC[1], stressors are conditions that may lead to human or ecological impairment or resource depletion. Stressor/impact chains can be developed by considering the energy, water, and raw material inputs to each life-cycle stage, as well as air, water, and solid waste emission outputs from each life-cycle stage. The inputs and outputs can then be compared against a list of potential impacts in order to develop stressor/impact chains. The development of stressor/impact chains is designed to focus the P^2 evaluation only on those stressors and associated impacts that are expected to change in one or more life-cycle stages as a result of implementation of a P2 activity. During the calculation of a specific P2 activity for a particular industry, only a subset of the criteria will be relevant. Furthermore, the stressor/impact chains discussed above may indicate that significant changes resulting from implementation of a P2 activity are only likely to occur during selected stages for a certain criterion. In addition, some criteria are relevant from an industry-average standpoint (i.e., when an entire industry is evaluated), and other criteria may only be appropriate when the P2 factor is determined from a site-specific standpoint (i.e., a single company at one location).

RESULTS

To demonstrate the usefulness of this preliminary framework, the lithographic printing industry was selected for a case study. Many different P^2 activities have been implemented by one or more of the seven lithographic printers that agreed to provide information for this project. The selection of a solvent substitute for blanket or press wash was selected for demonstration and is modelled after a specific printer that has made two changes in their blanket and press wash over a five-year period. Each change was designed to incorporate the use of reduced volatile organic compound (VOC) releasing solvents. The company started with 543 Type Cleaner in 1988, changed to Ultra Fast Blanket Wash 2215 in 1990, and made another switch to 1044 Press Wash in 1993.* Records were kept of the quantity of solvent used each year and the total sales increased by 61% over the five year period.

Based on the stressor/impact chain for this particular process, eight scoring criteria were selected in three life cycle stages; raw materials acquisition stage, materials manufacture (petroleum refining), and product fabrication (printing). These criteria (see Table 1) were selected from a larger list of scoring criteria because specific stressors are expected to change due to the decreased volatility of the blanket/press wash mixture. A ninth scoring criterion is available as a fall-back option for scoring stressors that cannot be readily quantified with available data. Since not all of the data are available for accurate scoring of every criterion in this example, hypothetical scores have been developed to demonstrate the calculation process for the original solvent wash and each substitute. The scores of all three solvents are shown in Table 2.

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

TABLE 1. SCORING CRITERIA FOR CALCULATION OF SOLVENT SUBSTITUTION

Raw Material Acquisition Stage

Resource Renewability

9	Renewability < 1 year
7	Renewability 1 - 10 years
5	Nonrenewable, sustainability > 500 years
3	Nonrenewable, sustainability 50 - 500 years
1	Nonrenewable, sustainability < 50 years
*	Insufficient data

Material Manufacturing Stage

Petroleum Refining - Energy Usage

9	< 5,000 BTU/lb
7	5,000 - 10,000 BTU/lb
5	10,000 - 20,000 BTU/lb
3	20,000 - 30,000 BTU/lb
1	> 30,000 BTU/lb
*	Insufficient data

Petroleum Refining - Airborne Emissions

9	< 20 mg/lb
7	20 - 200 mg/lb
5	200 - 500 mg/lb
3	500 - 2,000 mg/lb
1	> 2,000 mg/lb
*	Insufficient data

Petroleum Refining - Waterborne Effluents

9	< 1,000 mg/lb
7	1,000 - 2,000 mg/lb
5	2,000 - 3,000 mg/lb
3	3,000 - 5,000 mg/lb
1	> 5,000 mg/lb
*	Insufficient data

Product Fabrication Stage

Printing - VOC Emissions

9	< 20 mg/lb
7	20 -200 mg/lb
5	200 - 500 mg/lb
3	500 - 2,000 mg/lb
1	> 2,000 mg/lb
*	Insufficient data

Printing - Ozone Depleting Potential Relative to CFC-11

9	< 0.01 (all non-halogenated chemicals, HFC-125, HFC-134a, HFC-143a, HCFC-152a)
7	0.01 - 0.39 (HCFC-22, HCFC-123, HCFC-124, HCFC-141b, HCFC-142b)
5	0.40 - 0.69 (CFC-115)
3	0.70 - 0.99 (CFC-114)
1	≥1.00 (CFC-11, CFC-12, CFC-113, Carbon Tetrachloride, Halon-1301)
*	Insufficient data

Printing - Global Warming Potential Relative to CO_2 over 100 Years

9	<1 (H-2401, H-2311)
7	1 - 99 (CO_2, HCFC-123, H-1211, H-1202, H-2402, H-1201, Methane, HCFC-141b)
5	100 - 499 (Nitrous Oxide, HCFC-124, HFC-152a, Methyl Chloroform)
3	500 - 4,999 (CFC-11, CFC-113, Carbon Tetrachloride, HCFC-22, HFC-125, HFC-134a, HCFC-142b, HFC-143a)
1	>5,000 (CFC-12, CFC-114, CFC-115)
*	Insufficient data

Printing - Inhalation Toxicity

9	NOAEL > 1,000 mg/m^3 in air
7	NOAEL 10 - 1,000 mg/m^3 in air
5	NOAEL 0.1 - 10 mg/m^3 in air
3	NOAEL 0.01 - 0.1 mg/m^3 in air
1	NOAEL < 0.01 mg/m^3 in air
*	Insufficient data

Fall-Back Option where Data are Unavailable

Estimated Status Relative to Industry Norm

9	Much better (≥ 50% better)
7	A little better (25 - 50% better)
5	Equal to norm (±25%)
3	A little worse (25 - 50% worse)
1	Much worse (≤ 50% worse)

TABLE 2. HYPOTHETICAL EXAMPLE FOR SOLVENT SUBSTITUTIONS AT A LITHOGRAPHIC PRINTER

LCA STAGE/SCORING CRITERIA	CRITERIA SCORES		
	FIRST SOLVENT	SECOND SOLVENT	THIRD SOLVENT
RMA/Resource Renewability	3	3	7
MAN-MM/Energy Usage	3	5	3
MAN-MM/Airborne Emissions	5	7	7
MAN-MM/Waterborne Effluents	5	7	7
MAN-PF/VOC Emissions	5	5	7
MAN-PF/Ozone Depleting Potential	7	7	9
MAN-PF/Global Warming Potential	7	9	9
MAN-PF/Inhalation Toxicity	5	5	7
COLUMN TOTALS	40	48	54

RMA = Raw Materials Acquisition, MAN = Manufacturing Stage,
MM = Materials Manufacture, PF = Product Fabrication

Based on the sum of the individual scores, the first solvent switch would be rated 1.20 (48/40) while the second solvent switch would be rated 1.35 (54/40). These ratings can then be compared with other P2 activities for the lithographic printing industry. The higher the score, the lower the environmental impacts.

CONCLUSIONS

While the results of this application of the P^2/LCA framework to the lithographic printing industry are only preliminary and involve hypothetical data, the case study indicates good potential for evaluting P^2 options based on life-cycle considerations. The solvent changes made by this particular printer for the blanket wash were selected based on a single criterion, i.e., low VOC emissions, however, the additional, applicable life-cycle information for the new solvents indicates that these changes have effected overall environmental improvements as well.

REFERENCES

1. Fava, J.A., F. Consoli, R. Denison, K. Dickson, T. Mohin, and B.W. Vigon. A Conceptual Framework for Life-Cycle Impact Assessment. Workshop Proceedings. Society of Environmental Toxicology and Chemistry, Sandestin, Florida, 1992.

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Chemical Ranking for Potential Health and Environmental Effects

Between 60,000 and 100,000 of the over 8,000,000 chemicals listed by the Chemical Abstracts Services Registry are commercially produced. Each of these has the potential of becoming an environmental pollutant, but the time and resources required to perform thorough testing of the potential human health and environmental effects of chemical exposure can be prohibitive. Chemical ranking and scoring systems that evaluate the toxic effects of chemicals and have an exposure component are science-based screening tools that can rapidly assess relative chemical hazards. Several chemical ranking and scoring systems have been or are being developed for the purposes of regulatory action, priority setting or impact evaluation, but there currently is no scientific consensus on chemical ranking. Furthermore, many of the existing methods focus on a single environmental media, or have been demonstrated on only a limited number of chemicals.

The University of Tennessee Center for Clean Products and Clean Technologies developed a chemical ranking and scoring method under EPA Cooperative Agreement CR 816735, *The Product Side of Hazardous Waste Reduction: Evaluating the Potential for Safe Substitutes.* The method was designed as a priority-setting tool, to recommend a set of priority chemicals for substitute evaluation. The method provides an approximate ranking of chemical hazards based on their relative toxicity and potential for exposure. The method was demonstrated using the chemicals for which toxic chemical release reporting is made in the Toxic Release Inventory (TRI) as required under Section 313 of Title III of the Superfund Amendments and Reauthorization Act (SARA) of 1986 and high-volume pesticides selected from annual pesticide usage data.

In the development of the chemical ranking method, three areas were examined: 1) the availability of experimental data and what to do when experimental data are absent; 2) the formulation of scoring criteria which could be used to estimate the toxic effects of chemicals and the potential for exposure; and 3) the development of an algorithm that combines and weights these criteria in order to rank chemicals according to their potential human health and environmental effects:

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NMP-BASED COATINGS REMOVER AT TOOELE ARMY DEPOT

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INTRODUCTION

The goal of this study is to evaluate a replacement solvent paint remover for methylene chloride and other hazardous compounds that can be used to remove organic coatings, such as enamels, lacquers, and varnishes from metal surfaces. Methylene chloride is a primary component of many cold paint removers and is one of the substances targeted by the 33/50 Program for use reduction. U.S. EPA considers methylene chloride to be a hazardous air pollutant because of its low exposure limit and high volatility. The paint remover to be evaluated is based on n-methyl-2-pyrrolidone (NMP) and also contains monoethanolamine (MEA). NMP is a highly versatile solvent that has been used for more than 15 years in the chemical and petrochemical industries. MEA is used as a co-solvent that helps accelerate removal of paint and other organic contaminants.

Tooele Army Depot (TEAD) provided the site for this technology demonstration. TEAD is a government-owned, government-operated (GOGO) installation, located in Tooele, Utah since 1943. It is one of 12 depots and 6 depot activities in the Depot System Command (DESCOM). TEAD's primary function is to overhaul the Army's tactical wheeled vehicles and associated secondary items, including trucks, trailers, engines and transmissions. TEAD also overhauls and repairs many other types of troop support equipment, including generators, topographical and surveying equipment, and reproduction equipment. TEAD has been designated by DESCOM as the Center of Technical Excellence for the High Mobility Multipurpose Wheeled Vehicle (HMMWV), the Heavy Expanded Mobility Tactical Truck (HEMTT) and other tactical wheeled vehicles.

The focus of this study is on the Parts Chemical Cleaning System (PCCS), which is designed for depainting, cleaning and applying conversion coatings to ferrous and nonferrous engine parts and powertrain subassemblies. Only the nonferrous cleaning line was the subject of this study. Application of conversion coatings is a surface preparation method to provide corrosion protection and increase adhesion of the paint coating.

PCCS is designed such that an automated overhead monorail transports baskets of parts through tanks of paint remover and various rinses, prior to application of conversion coatings. A preprogrammed system controls the process by controlling the material handling equipment that immerses the baskets into the tanks for predetermined dwell times, drains the baskets, and moves the baskets to succeeding tanks. The rinsewater from the process contains paint remover, dissolved paint resins, pigments, and other paint additives. This rinsewater is piped into a holding tank and then is later treated by a fixed-film biological reactor prior to merging it with a stream that feeds to the Industrial Waste Treatment Facility. The system employs automatic controls to regulate tank solution levels, temperatures, agitation tank ventilation, tank heating and solution filtration.

This study evaluated three objectives. First, the study evaluated the ability of the replacement paint remover to remove paints and compared these results with those using the old technology (methylene chloride). The pollution prevention potential of the new paint remover and rinsewater purification system were evaluated. Finally, the economic potential of the new paint removal process was compared to the cost of using the methylene chloride paint removal system.

METHODOLOGY

To evaluate product quality, test coupons were made and processed through the paint remover system along with actual parts. An equal number of coupons were coated with heat resistant or chemical agent resistant coatings. The degree of paint removal from the coupons was qualitatively evaluated. The baskets of actual parts were evaluated on a pass/fail basis. To evaluate the pollution prevention potential of the new paint remover solvent system, three process streams will be evaluated. First, the paint removal solvent was evaluated for dissolved metals (Cd, Cr, Cu, Pb, Mn, Ni, and Zn) and concentrations of NMP and MEA. The rinsewater entering the biological reactor was analyzed for concentrations of metals, NMP, MEA, pH, total suspended solids, total organic carbon, and chemical oxygen demand. The rinsewater was also analyzed after treatment by the biological reactor for the same analytes.

RESULTS

Data was still being compiled at publication of this extended abstract. Qualitative analysis of the test coupons and parts batches indicates that the NMP-based solvent removed the paint as well as the methylene chloride paint removal system. Results of the study will be presented at the Symposium

SELECTED TECHNOLOGY ASSESSMENTS AND EVALUATIONS UNDER THE WREAFS PROGRAM

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INTRODUCTION

As Federal environmental objectives are identified for the 1990's, EPA programs are being restructured to meet new requirements. Chief among these is the increased importance of pollution prevention in all Federal activities. Further, all Federal departments and services have been directed to develop pollution prevention opportunities in order to decrease the environmental burden resulting from Government activities, and to provide opportunities in both the public and private sector to reduce environmental risks.

In keeping with the Agency's responsibility to advise and cooperate with other Federal departments on environmental risk reduction, the Pollution Prevention Research Branch (PPRB) has managed a technical support effort knownas the Waste Reduction Evaluations At Federal Sites (WREAFS) Program.

METHODOLOGY

The WREAFS Program was established to conduct research, develop and demonstrate opportunities to reduce the generation of waste from Federal activities. Since 1988, WREAFS has funded work on other Federal sites and it has supported RD&D with other Federal departments through Interagency Agreements (IAG). WREAFS has sponsored pollution prevention opportunity assessments, base-wide assessments, technology and product demonstrations, technology evaluations, technology and methodology development, technical assistance and technology transfer across the Federal community.

WREAFS has conducted cooperative RD&D activities with the following Federal departments and services:

National Aeronautics and Space Administration,
Department of Defense,
Department of Treasury,
Department of Transportation,
Department of Energy,
Department of Interior,
Department of Agriculture,
Department of Veterans Affairs,
U.S. Postal Service.

WREAFS continues to provide integrated environmental support for: (1) primary research in pollution prevention technology; (2) expanding cooperative research, development and demonstration with other Federal departments; (3) developing technology transfer opportunities for both public and private sector benefit. This presentation will discuss recently completed WREAFS projects, highlighting the following two technology evaluations:

NASA-LaRC Dry Powder Towpreg Technology Evaluation

One WREAFS project focused on the production of non-refractory composite materials and aircraft structures made from those materials. Basic composites are graphite or carbon fibers impregnated with some type of polymer - a process called, "prepregging." In solution prepregging, polymer resin is placed in a solvent carrier and applied to the fiber. The solvent volatilizes off as toxic air emissions. Polymer resins normally have a self life and must be refrigerated until the solvent carrier has been extracted.

NASA-LaRC's Polymeric laboratory has developed a process called, "Dry Powder Towpreg", in which the fiber stands are separated in a small air chamber and a finely-powdered polymer resin is "dusted" onto them. The polymer dust fully impregnates the fibers just before being passed through a furnace. The resulting composite "ribbon" is allowed to cool. Later, it can be formed into a laminate and used in composite manufacturing without requiring changes in capital equipment for application. This process has the potential to eliminate the use of solvents, and reduce energy consumption because in dry powder form polymer resins do not require refrigeration.

For this technology evaluation, EPA compared the solution and dry powder processes, using methyl ethyl ketone to demonstrate solvent reduction for thermosets and n-methyl-pyrrolidone for thermoplastics. The test was designed to evaluate the performance of the dry powder process and to determine the environmental and energy impacts of each process.

MEK Substitute in Aircraft Radome Depainting

For this project, WREAFS has researched and evaluated substitutes for methyl ethyl ketone (MEK) as cleaners and solvents in aircraft maintenance operations at Tinker Air Logistics Center (ALC) in Oklahoma. Tinker ALC performs maintenance, including structural repair and re-fabrication of USAF aircraft, notably the B-1B and the B-52. Tinker ALC reported using MEK at an annual rate of 5,385 gallons to wipe-down aircraft, and 8,250 gallons to depaint aircraft radomes.

From its research and through a CRADA with Texaco, RREL identified solvent formulations based on propylene carbonate and n-methyl pyrrolidone as possible alternatives for MEK. Three formulations were tested as proof-of-concept, using test coupons from condemned radomes. The test focused on the ability of the chemical mixture to accomplish the job required, and meet the same MILSPEC standard as MEK without modifying the operational procedures.

This study determined that a blend of 25% propylene carbonate, 50% n-methyl pyrrolidone and 25% Dibasic ester (PC blend) removed paint in comparable time to the MEK, although a little more scrapping was required for final removal. Hardness tests showed that the PC blend did not embrittle the fiberglass/epoxy substrate of the radome, nor did it effect flexural properties. Scanning with electron microscope indicated no significant damage to the fibers or fiber matrix interface. Test samples were successfully re-painted and demonstrated complete paint adhesion. For solvent properties, the PC blend compares favorably with MEK. The PC blend has a flash point of 210OF (against MEK's 20OF), low toxicity, and lower evaporation rate.

CONCLUSION

Many of the WREAFS projects are selected on the basis of a pollution prevention technology or technique's ability to prevent or reduce compliance problems at Federal facilities. It is

anticipated that the continuing compliance responsibilities of Federal facility operators will merge with cleaner operating practices. That is, facility managers are looking for ways to avoid producing wastes that require controlled disposal, and for clean substitutes for toxic chemicals, some of which are being banned. In response, WREAFS is developing initiatives to integrate pollution prevention with environmental compliance. In this environment, WREAFS will develop opportunities for cutting edge RD&D and innovative technologies, driven by the compliance incentive.

RECYCLING NICKEL ELECTROPLATING RINSE WATERS

BY LOW TEMPERATURE EVAPORATION AND REVERSE OSMOSIS

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INTRODUCTION

Electroplating operations generate rinse water wastes that are classified as hazardous due to the presence of heavy metals. Typical metals and alloys used for plating include cadmium, copper, iron, lead, nickel, gold, silver, platinum, brass and bronze. Rinse water wastes can be treated by either end-of-pipe or in-plant recovery techniques. End-of-pipe treatments rely on chemical reactions such as pH adjustment to precipitate metal and other plating chemicals. These methods provide an effective means to remove the metal and cyanide species from the rinse water thus enabling reuse or discharge of the water. However, in most plant treatment systems, waste streams from the various plating lines are combined prior to treatment. Consequently, the resulting sludge must either be disposed of or treated with a high temperature metals recovery system to recover the metals. These options tend to be wasteful and expensive to implement.

Low-temperature evaporation and reverse osmosis techniques were each evaluated (on a pilot scale) on their ability to process rinse water collected from a nickel electroplating process. This project was done in cooperation with Graham plating in Chicago, Illinois. The testing was conducted at HWRIC's pilot scale laboratory.

METHODOLOGY

Low temperature evaporators(LTE) manufactured at Licon, Inc., in Pensacola, FL heat water under a vacuum to produce steam at relatively low temperatures (150 to 160° F). The steam rises into a condenser where distilled water results. The plating bath chemicals do not rise with the steam and become a concentrated slurry or solution of chemicals. The LTE unit is a model C-3, single effect, pilot scale evaporator especially designed for conducting pilot scale tests on a variety of feed solutions.

Reverse osmosis(RO) is a pressure-driven membrane separation process in which a feed stream under pressure (200 to 800 psi) is separated into a purified "permeate" stream and a "concentrate" stream by selective permeation of solution through a semi-permeable membrane. The

pressure required to force the permeate through the membrane is dictated by the osmotic pressure of the feed stream. Membranes are constructed of a variety of materials such as aromatic polyamide, cellulose acetate, and polyether/amide. The RO unit used in this project was an Osmonics model PES/OSMO-19T-80SSXXC reverse osmosis machine for process evaluation. It was equipped with one Osmonics model number 192T-MSO5 thin-film, composite, spiral-wound membrane cartridge. The solution was prefiltered through a 5 μ cartridge filter for the RO testing.

Four, 55-gal drums of nickel electroplating rinse water were collected from the Graham Plating facility and processed through the LTE(Drums A and B) and the RO (Drums C and D) systems. The RO tests were conducted at two different operating pressures: Drum C at pressures of 250 to 300 psi and Drum D at 350 to 380 psi. Samples of the concentrated feed solution as well as the distillate (LTE system) and permeate (RO system) were collected at regular intervals throughout the tests as the rinse water was processed. Nickel analyses were done to determine how efficiently the systems removed nickel from the rinse water and concentrated it for potential recycling. Analyses for total organic carbon (TOC) were done to indicate the fate of organic constituents (e.g., brighteners) in the rinse water. Immediately after samples were collected, electrical conductivity measurements were made to indicate the soluble salts present in the samples.

RESULTS

The LTE system concentrated the rinse water, which had exhibited initial nickel concentrations of 2,540 to 4,140 mg/L to nickel levels as high as 13% to 18%. These levels are well above the 8% required for placement into the plating bath. The concentrate, permeate, and distillate nickel concentrations exhibited in samples collected throughout the tests have been summarized (Table 1). Nickel concentrations increased at a steady rate until concentrations of approximately 25,000 to 30,000 mg/L were reached. Figure 1 shows how nickel levels changed in the feed solution during the course of the low temperature evaporation tests. This level corresponds to a point where approximately 80% to 85% of the rinse water volume had been processed. Beyond this point, nickel concentrations increased dramatically until the final concentrations of 13% and 18% were achieved. The rinse water feed solution volume was reduced by over 98% as a result of this process.

Table 1. *Comparison of Nickel Concentrations in Concentrate, Distillate, and Permeate*

	Low Temp. Evap.		*Reverse Osmosis*	
Product	*Drum A*	*Drum B*	*Drum C*	*Drum D*
Concentrations at beginning of test (mg/L):				
Concentrate	*4,140*	*2,540*	*2,580*	*1,425*
Distillate	*2.5*	*2.2*	—	—
Permeate	—	—	*44.5*	*14.5*
Concentrations at end of test:				
Concentrate	*179,000*	*128,000*	*12,560*	*18,200*
Distillate	*1*	*0.3*	—	—
Permeate	—	—	*210*	*790*
Ratio of distillate permeate to concentrate:				
Distillate	*0.02%*	*0.01%*	—	—
Permeate	—	—	*1.49%*	*1.54%*

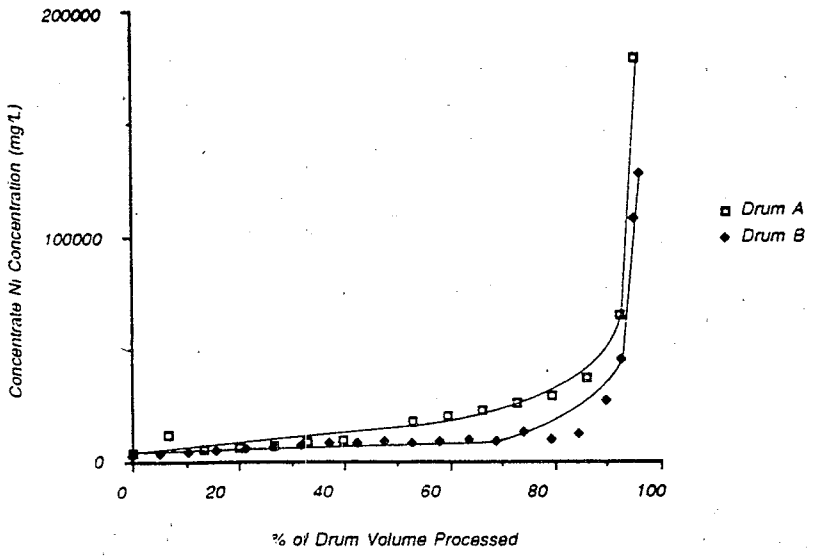

Figure 1. Concentrate nickel concentration versus percent of drum volume processed; LTE tests.

The LTE system concentrated the organic constituents of the rinse water from initial TOC levels of 550 to 990 mg/L to final levels of 25,000 to 26,000 mg/L. TOC levels in the Graham Plating nickle baths are normally maintained at approximately 14,000 mg/L. The concentration rate of the organic components paralleled the nickel concentration rate suggesting that little of the organic material was lost to volatization. As shown in Table 2, distillate produced by the LTE system was very low in nickel concentration (average 0.37 to 0.71 mg/L). Additionally, TOC concentrations in the distillate were very low (average 3.04 to 3.50 mg/L). Disadvantages of the LTE system include its relatively high ($140,000) capital cost and high energy requirements ($20/ 1,000 gal processed). The implied rate of return of 10.6% and payback period of 6.9 yr determined in the economic assessment for this system suggest that it is a marginal investment opportunity by today's standards. These estimates do not, however, consider the reduced future liabilities brought about by drastically decreasing the hazardous waste discharges from the facility.

The feed solution processed through the RO system contained initial nickel concentrations of 1,425 to 2,580 mg/L (Table 1). Figure 2 depicts how nickel concentrations in the feed solution changed as the solutions were processed. Nickel concentrations increased steadily until about 60% of the rinse water volume was processed. At this point, nickel concentrations were about 4,000 to 5,000 mg/L in the two drums. Beyond this point, nickel concentrations increased more rapidly until final concentrations of 12,560 mg/L (Drum C) and 17,900 mg/L (Drum D) were reached. The RO system exhibited superior productivity at the beginning of the tests and productivity dropped off dramatically after about 60 % of the feed solution had been processed. Beyond these levels, the productivity of the RO equipment decreased dramatically as solids began to precipitate and foul the membrane. The final concentrations achieved with the RO process were 12,560 to 18,200 mg/L (1.256% to 1.82%) and are well below the 8% nickel concentration required for the plating bath. Some of this solution could be used to replace water losses in the electroplating process. The RO system, however, would probably produce excess volumes of concentrated rinse water composed of 1.2% to 1.8% nickel. This material would have to be further processed with the use of an alternative technology such as LTE or be shipped to a facility that could extract the nickel for use in other industrial processes.

The RO system concentrated the organic constituents present in the rinse water feed solution from initial TOC levels of 340 to 540 mg/L to levels of 2,800 to 3,500 mg/L. These concentrations suggest that the organic bath constituents are concentrated by the reverse osmosis equipment at rates

that parallel the nickel concentration rates. The quality of the cleaned rinse water permeate produced by the RO equipment was directly related to the quality of the feed solution pumped into the unit. Permeate produced by the reverse osmosis system averaged 89 to 134 mg/L nickel (Table 2). These levels are about 98.5% lower than the nickel concentrations present in the concentrated solution. This solution would not, however, be acceptable for discharge to publicly owned treatment works.

Table 2. Average Nickel Concentrations in Distillate and Permeate

	Distillate Ni Concentration		Permeate Ni Concentration	
	Mean (mg/L)	Standard Deviation (mg/L)	Mean (mg/L)	Standard Deviation (mg/L)
A (n=13)	0.71	0.63	—	—
B (n=16)	0.37	0.52	—	—
C (n=22)	—	—	89.55	49.22
D (n=17)	—	—	134.38	202.19

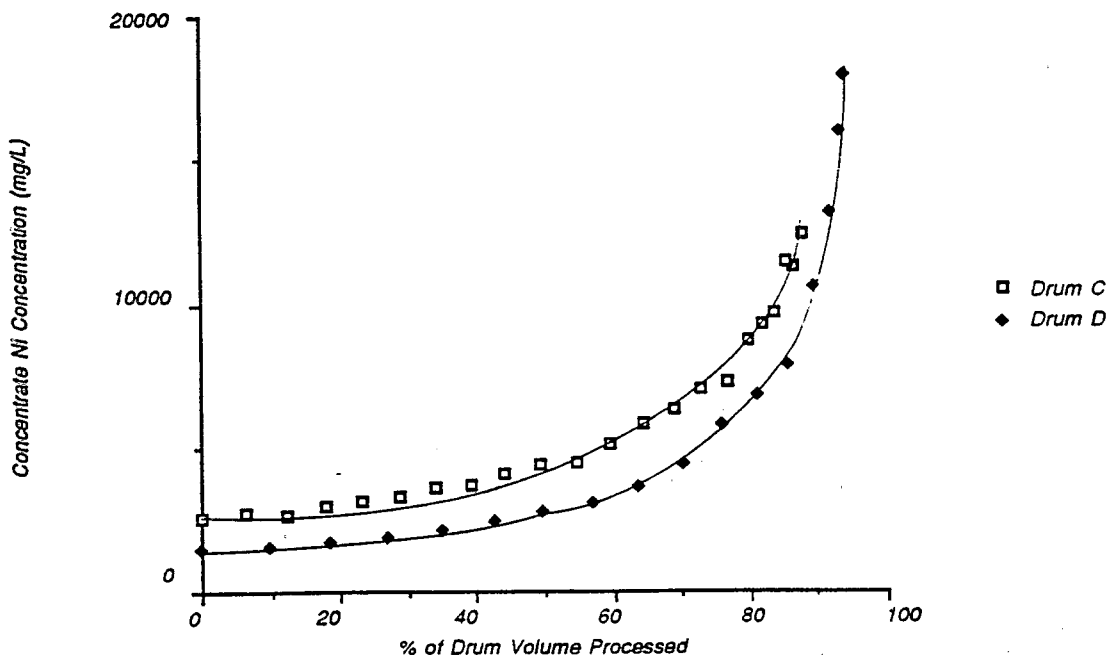

Figure 2. Concentrate nickel concentration versus percent of drum volume processed; RO tests.

The nickel levels present in this solution could be further reduced by passing this solution through the reverse osmosis equipment again. TOC concentrations averaged 19.46 to 21.98 mg/L in the permeate solution which suggests that some of the organic compounds were able to permeate the membrane. The reverse osmosis equipment condensed the feed solution to final volumes that were 88% to 94% less than the original volumes of the two tested drums. Differences between the two tests can be attributed to the difference in operating pressures used during the tests. Advantages of the RO system include its relatively high production rates with respect to low concentration feed solutions. Additionally, it would require lower capital investment (about $50,000) than a comparably sized LTE system. Energy costs required to operate a RO system would be only about $2.50/1,000 gal processed. Disadvantages associated with a reverse osmosis system include its inability to concentrate the feed solution to levels beyond the 12,560 to 18,200 mg/L levels revealed in this study. This factor alone would prevent use of a stand alone reverse osmosis system at the Graham Plating facility because of the economic impracticalities associated with the concentrate produced by the system. Another disadvantage associated with the RO system is the lower quality permeate produced by the system. This solution would probably have to be reused within the plant or further processed through the reverse osmosis system before discharge to the POTW.

Both the LTE and RO systems appear to offer advantages under specific operating conditions. Based on this factor, the potential for utilizing these technologies in tandem was examined. The RO system is best adapted to conditions where the feed solution has a relatively low nickel concentration. It can process the low concentration feed solution with relatively high efficiency to a level of 4,000 to 5,000 mg/L. At this point, the solution could be transferred to the LTE for further concentration. The LTE system appears to be best adapted to processing solutions with relatively high nickel concentrations. It can process these solutions so that a concentrate solution composed of 8% or more nickel is produced along with a very high quality distillate solution. Using the equipment within its optimum operating ranges would augment the ability of the systems to process the rinse water with maximum efficiency while supplying the electroplating operation with high quality concentrate, distillate, and permeate solutions for reuse. Since the equipment would always be functioning within optimum concentration ranges, smaller reverse osmosis and low temperature evaporation units could be implemented than if the individual units were used alone. If this type of combined system were installed at the Graham Plating facility, it would require a capital investment of $115,000 which would be paid back in 2.8 yr through a 27.6% implied rate of return.

Electrical conductivity measurements taken during operation of both the low temperature evaporation and reverse osmosis systems could be of great value during actual plant operating conditions. The electrical conductivity data obtained in this project were well correlated with nickel concentration, TOC concentration, and membrane flux characteristics.

CONCLUSIONS

This research evaluated LTE and RO systems on a pilot scale basis to tests their respective ability to process rinse water collected from a nickel electroplating operation. Each system offered advantages under specific operating conditions. The LTE system was best suited to processing solutions with relatively high (greater than 4,000 to 5,000 mg/L) nickel concentrations. The RO system was best adapted to conditions where the feed solution had a relatively low (less than 4,000 to 5,000 mg/L) nickel concentration. In electroplating operations where relatively dilute rinse water solutions must be concentrated to levels acceptable for replacement in the plating bath, a combination of the two technologies might provide the best process alternative. Initially, the RO system could be used to concentrate the feed solution. This could be followed by LTE processing to concentrate the solution to levels acceptable for replacement in the plating bath.

For more information on this study or other pollution prevention research studies contact the U.S.EPA Pollution Prevention Research Branch (513-569-7215) or Paul Randall (513-569-7673).

SOURCE REDUCTION IN THE PULP AND PAPER INDUSTRY

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SOURCE REDUCTION REVIEW PROJECT

The Source Reduction Review Project (SRRP) is an initiative of the U.S. Environmental Protection Agency to evaluate pollution prevention alternatives during the regulatory development process. The goal of the SRRP is to foster the use of source reduction measures as the primary means of achieving compliance. At present the SRRP is focusing its efforts on regulatory development within the Agency's Office of Water, Office of Air and Office of Solid Waste. The Office of Research and Development (ORD) is working with these program offices, as well as the Office of Pollution Prevention and Toxics and the Pollution Prevention Policy Staff, Office of the Administrator.

The Risk Reduction Engineering Laboratory (RREL), ORD, is working on issues primarily related to the Office of Water and the Office of Solid Waste. The primary focus of the SRRP-related Industrial Wastewater Program is on industrial sectors that have been identified by the Office of Water. These include the pulp and paper industry, the pesticide formulating, packaging and repacking industry, the pharmaceutical industry and the metals and metal products industry. At present, there are active research projects ongoing in all but the metals and metal products industry.

PULP AND PAPER INDUSTRY

As outlined by the Environmental Defense Fund and the National Wildlife Foundation settlement agreement, the Agency is investigating process changes and pollution prevention strategies for the pulp and paper industry. A sampling effort has been completed at a pulping plant in Alabama. The Agency sampled this plant's pulping, bleaching and wastewater treatment technologies. Included in this evaluation was the Kamyr, or extended cooking process, which is a pollution prevention technology because it focuses on removing lignin from pulp prior to bleaching. This increases the quantity of organic material recycled and burned in the recovery boiler for energy recovery rather than being removed in the bleach plant as in the conventional process. The extended cooking process also decreases the amount of bleaching chemicals required, thereby reducing the likelihood of forming and discharging chlorinated organics. The key analytes of concern are volatile organics, chlorinated dioxins and furans, chlorinated phenolics, adsorbable organic halogens (AOX), organic halides (OX), COD, BOD, TSS and color. Based on the samples collected, the dioxin and furan results indicate very low "hits" (all liquid samples were 11 parts per quadrillion or less; the sludge samples were detected at 1.0 parts per trillion or less). There were sporadic "hits" of chlorinated phenolics in the pulp line and final effluent, but a review of plant operating data indicates a discrepancy with these values.

A brief sampling effort at a pulp and paper plant in Virginia to characterize this plant's pulping, bleaching and wastewater treatment technologies has been completed. This plant has incorporated an ozone system for its bleaching process as a substitute for chlorine. By using an oxidant such as ozone rather than chlorine, the likelihood of forming and discharging chlorinated organics is eliminated. This study was conducted jointly with the Office of Air to evaluate the effects of ozone bleaching in both the aqueous and air media. However, the air analysis portion of this program was completed by making an estimate of air emissions based upon contaminant concentrations determined in water and slurry samples.

Over the past three years, ORD and the Office of Water have jointly investigated novel pollution prevention processes within the pulp and paper industry. These processes have included oxygen delignification, extended cooking, and ozone bleaching. The investigation of

Totally Chlorine Free pulping processes is another classic pollution prevention technology that will be targeted for investigation by ORD. This technology is based on using oxygen, peroxide, and other reagents to achieve a pulp with comparable strength and brightness as chlorine-bleached pulp. The European and Nordic nations currently lead-the-way in investigating these technologies along their bleach lines.

PESTICIDE TREATABILITY DATA BASE, VERSION 2.0

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PESTICIDE TREATABILITY DATA BASE, VERSION 2.0

As a result of amendments to the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA '88), the U.S. Environmental Protection Agency (EPA) no longer accepts stockpiles of pesticides that have been suspended or canceled, but reviews instead the pesticide manufacturer's proposed disposal methods. In ongoing studies of various problems associated with pesticide disposal, the EPA has identified and categorized treatability data and disposal methods for various pesticides. The Pesticide Treatability Data Base was created for use by the Office of Prevention, Pesticide and Toxic Substances (OPPTS) and for others to use to disseminate this important information.

The Pesticide Treatability Data Base lists more than 1500 pesticides currently in use in the United States or removed from the market in the last 20 years. Physical and chemical properties of the compounds, treatability data, Freundlich isotherm data, and other names by which the pesticides are known are listed, when available, as well as complete references for the sources from which the data were derived.

A thorough search was performed of all available reference material and scientific and technical journal articles concerning the general characteristics of pesticides and the treatability/destruction of pesticides. All reference material retrieved was reviewed and all chemical and physical data concerning the pesticides were transferred to a standardized form. These standardized forms were used by a technician to transfer the information from the reference material to the data base.

All treatability/destruction selections were reviewed to ascertain if the appropriate technical information was included. The technical information required included:

- Experimental procedures
- Influent levels
- Effluent levels or percentage of chemical removed

Once the appropriate information was retrieved from each article, the data were placed on standardized forms and entered by a technician. A stringent Quality Assurance/Quality Check system was devised and strictly adhered to in order to maintain accurate transfer of data.

The Pesticide Treatability Data Base allows access to information on the user's own PC. The data base program can run on any version of DOS and is assembled in such a "user-friendly" way that anyone with even the most basic knowledge of computers can access the information successfully, saving valuable time and resources.

Upon successful completion of the installation of the program and data base files, the data base can be accessed. Due to the fact that each active ingredient can have a variety of names, the data have been made accessible to searches using any of the following information:

- Compound name
- Chemical Abstract Service (CAS) number
- Trade names and synonyms

Once one of the above options is chosen, for example entering "malathion" under compound name, the program will give you choices to print the report, display the report, or return to main menu. Choosing the "display" option allows the user to view the first screen (Table 1). This screen provides the chemical/physical data for the active ingredient.

```
Version 2.0 Pesticide Treatability Data Base                    09/29/92
Search on:  MALATHION
DIMETHYL PHOSPHORODITHIOATE OF DIETHYL MERCAPTOSUCCINATE, O,O-

CAS Number............:  121-75-5  Pesticide Compound Code..:  05770
Compound Class........:  I
Compound Formulation..:  D, EC, OS, P, ULV C, WP
Molecular Formula.....:  C10-H19-06-P-S2
Compound Type.........:  OP

CHEMICAL AND PHYSICAL PROPERTIES                                REFERENCE

Physical Form.............:  L                                    0008
Molecular Weight(g/mole)...:  330.38                              0514
Melting Point(C)...........:  2.9                                 0509
Boiling Point(C)...........:  156 TO 157                          0526
Vapor Pressure @T(C),TORR..:  4E-05 @ 30                          0526
Solubility in Water @T(C),mg/L.........:  145                     0509
Solubility in other solvents...........:  MOST ORG                0008
Stability..............................:  H:DEC @ HIGH TEMP       0002
Log Octanol/Water Partition Coefficient:  2.89                     512
Henrys Law constant,atm x m3mole-1.....:  NA                        NA

F2-Reference Search        F4-Abbreviations
F8-Print search            F9-Exit search          PgDn-Next screen
```

TABLE 1. FIRST SCREEN

As shown at the bottom of Table 1, the function keys are provided to allow the user to perform a reference search (F2), define the abbreviations used (F4), print the present search (F8), or exit to the main menu (F9). The user can now page down to the next screen which is the treatability data (Table 2).

Version 2.0 Pesticide Treatability Data Base
Search on: MALATHION 09/29/92

Treatment Technology Data

Technology	Source Matrix	Scale	Influent Level	Influent Units	Effluent Level	Effluent Units	Percent Improv.	Ref
Fil	RCRA	F	81.7	mg/L	0	mg/L	100C	0206
HT	WOS	B	1.00	g/L	0C	g/L	100	0325
GAC	C	P	60	mg/L	0	mg/L	100C	0206
GAC	C	P	100	mg/L	0.9	mg/L	99.1C	0206
GAC	C	P	20	mg/L	1	mg/l	95C	0206

NOTE: C - calculated value

F2-Ref Search F3-Treatment Technology F4-Other Abbrev.
F5-SIC Code List F10-to continue

TABLE 2. EXAMPLE DATA SCREEN

The user can hit F3 to define the "Treatment Technology" abbreviations used, for example "GAC" is defined as Granular Activated Carbon. Other abbreviations can be looked up by hitting the other function keys provided. By using the F10 key, the user will scroll through the data until the page down option is available to view the Isotherm Screen (Table 3).

Version 2.0 Pesticide Treatability Data Base 09/29/92
Search on: MALATHION
DIMETHYL PHOSPHORODITHIOATE OF DIETHYL MERCAPTOSUCCINATE, O,O-

FREUNDLICH ISOTHERM DATA

Absorbent	Matrix	K	1/N	C Units	X/M Units	Reference
MLSS	CLW	403	0.6	ug/L	ug/gm	0129

F2-Reference Search F4-Other Abbrev. PgUp-Previous screen
F5-SIC Code List F8-Print search F9-Exit search

TABLE 3. EXAMPLE ISOTHERM SCREEN

At this point the user will have seen all the data and may wish to find out where the data came from. By pushing F2 and typing the reference number of the data one is interested in, a reference screen will appear (Table 4).

Reference number: 0129

REFERENCE #0129: WEBER, W.J., Jr. and Jones, B.E., "Toxic Substance Removal in Activated Sludge and PAC Treatment Systems", EPA Report No.: EPA 600/S2-86/045, EPA Water Engineering Research Laboratory,Cincinnati, OH (June 1986).

All data on table for activated sludge were from systems operated at:

SRT = 6 days
HRT = 5.5 hours
MLSS = 3500 mg/L

Additional data available in reference at other SRTs and MLSSs. Data also available on partitioning of pollutants to air and sludge.

Data in table for PACT were from systems operated at:

SRT = 6 days
HRT = 5.5 hours
MLSS = 3900 mg/L (excluding PAC)
PAC = 50 mg/L of Hydrodarco C

with two exceptions:

Lindane
SRT = 3 days
MLSS = 2100 mg/L

Toluene
PAC = 200 mg/L

Additional data available in reference at other PAC dosages.

END OF DATA

TABLE 4. SAMPLE REFERENCE SCREEN

At this point the user can print the reference or return to the data screen and print the report. The data base is an excellent source of information for government researchers, regulators, pesticide user groups, pesticide producers, industry experts, and academia. The Pesticide Treatability Data Base can be obtained by writing to T. David Ferguson, Project Officer at the following address:

U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
26 West Martin Luther King Drive
Cincinnati, OH 45268

THE ECO LOGIC GAS-PHASE CHEMICAL REDUCTION PROCESS

Gerard W. Sudell
Foster Wheeler Enviresponse, Inc.
Raritan Plaza I - Second Floor
Edison, NJ 08837-3616
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513-569-7684

INTRODUCTION

The Eco Logic International (ELI) Gas-Phase Chemical Reduction Process treats organic hazardous waste in a hydrogen-rich reducing atmosphere at approximately 900°C and ambient pressure. The reaction products include hydrogen chloride (HCl) from the reduction of chlorinated organics such as polychlorinated biphenyls (PCBs), and lighter hydrocarbons such as methane and ethylene from straight-chain and aromatic hydrocarbons. Water acts as a hydrogen donor to enhance the reaction. The absence of free oxygen in the reactor inhibits the formation of dioxin and furan compounds. The first five reactions, through hydrogenation, remove chlorine from PCBs and reduce the higher molecular weight hydrocarbons to simpler, more saturated compounds. The final reaction regenerates hydrogen. When treating high concentration organic wastes, the ELI Process produces excess reformed gas. It can compress the reformed gas and store it for later use, either as fuel to fire the boiler, or as a fuel product for resale. A portion of the reformed gas is burned in a propane-fired boiler before release to the atmosphere.

Figure 1 shows a process schematic diagram of the field demonstration unit. The demonstration-scale reactor is 2 m (6 ft) in diameter and 3 m (9 ft) tall, mounted on a 15 m (45 ft) drop-deck trailer. ELI designed the unit to treat 4 tons/day of waste oil, 10 tons/day of wastewater, and 25 tons/day of gas/water vapor, depending on the nature of the contaminants, their degree of chlorination, and their water content. A thermal desorption unit or TDU, designed to remove most volatile, most semivolatile, and some metallic contaminants—treats the soil. A screw feeder delivers the contaminated soil to the TDU, which is swept with hydrogen to chemically reduce, or prevent the oxidation of volatile and semivolatile species created during soil heating. The contaminant-laden hydrogen stream flows to the reactor vessel. Decontaminated soil exits the desorber to a quench tank for proper disposal.

The reactor utilizes mixing, temperature, and residence time to convert the contaminants into a raw fuel gas. Nozzles spray steam-atomized waste liquid with associated suspended solids and PCB-rich oils into the reactor. For the Demonstration, a heat exchanger converted contaminated aqueous feedstock into atomized steam and heated liquor. The tangential entries swirl the reactants to provide effective mixing. The swirling mixture travels in the annulus formed by the reactor wall and a central ceramic tube past electrical heaters. By the time the mixture leaves the reactor, it has been heated to 900°C (1,650°F). The reduction reactions occur as the gases travel from the reactor inlet to the scrubber inlet.

After quenching, the gases flow through a countercurrent packed scrubber where contact with scrubber water removes hydrogen chloride and fine particulates. A large water-sealed vent, acting as an emergency

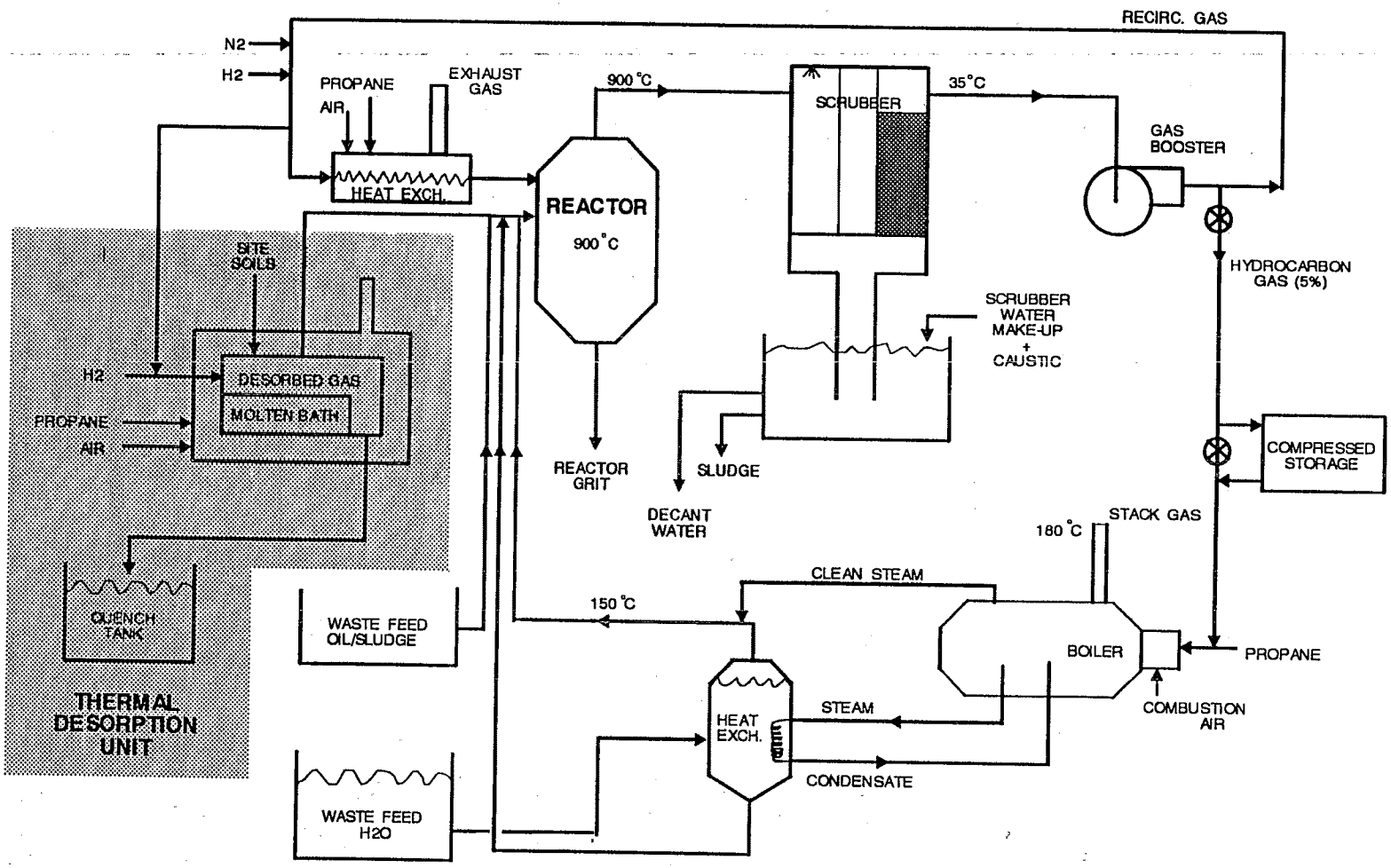

Figure 1. Reactor system and TDU diagram.

pressure relief duct, passes scrubber water to a tank below. A heat exchanger, fed by cooling water from an evaporative cooler, lowers the scrubber water temperature to 35°C (95°F). Caustic and makeup water, added to the scrubber liquor, maintain HCl removal efficiency. The scrubber produces two effluent streams: sludge and decant water.

Gases exiting the scrubber contain excess hydrogen, lighter hydrocarbon reduction products such as methane and ethylene, and a small amount of water vapor. Approximately 95 percent of this gas, reheated to 500°C (930°F), recirculates back into the reactor; about 5 percent of the hydrocarbon-rich gas serves as supplementary fuel for a propane-fired boiler. The boiler produces steam used in the heat exchanger, and polishes the reformed gas prior to emitting it; it produces the only air emissions.

METHODOLOGY

In preparation for the Demonstration, ELI first processed clean sand to adjust the system to peak performance, followed by feed containing a tracer material to adjust sampling equipment and sampling trains. Two test runs (Conditions 1 and 3) followed over the next 17 days. Condition 1 treated 2.3 tons of wastewater contaminated with 4,600 ppm of PCBs and 3,665 ppm of perchloroethylene (PCEs). Condition 3 treated 0.8 tons of waste oil contaminated with 24.5 percent of PCBs and 5,000 ppm of PCE. Condition 2, which EPA regarded as a proof-of-concept test, processed PCB-contaminated soil through the TDU; desorbed gases travelled to the reactor for further treatment. The two Condition 2 runs extended over nine days, treating 1.1 tons of soil contaminated with 650 ppm of PCBs and 15,240 ppm of hexachlorobenzene (HCB).

The SITE Demonstration Program objectives were as follows:

- Demonstrate at least 99.9999% destruction and removal efficiency (DRE) for PCBs.
- Demonstrate at least 99.99% destruction efficiency (DE) for PCE in the liquid feedstock.
- Ensure that dioxin and furans were not formed.
- Characterize products of incomplete reaction (PIR) emissions.
- Characterize HCl emissions.
- Document compliance with Michigan Department of Natural Resources (MDNR) air permit.
- Characterize criteria air pollutant emissions.
- Document compliance with Toxic Substances Control Act (TSCA) permit requirements.
- Validate cost assumptions used in economic analyses.
- Characterize effluents and residual streams relative to disposal requirements.
- Determine the suitability of the reformed gases for reuse/resale.
- Demonstrate system reliability.
- Develop a system mass balance, including metals.
- Characterize critical process scale-up parameters.
- Validate the ELI Chemical Ionization Mass Spectrometer (CIMS).
- Document system operation during test runs.

Sampling and analysis of the feedstock, intermediate products, and residual streams followed standard EPA procedures outlined in the Demonstration Plan. EPA subjected the entire sampling and analysis program to a rigorous Category II quality assurance (QA) procedure designed to generate reliable test data. The Demonstration Plan details the QA procedures.

EPA sampled three matrices—gas, solid, and liquid—and analyzed all key input, intermediate, and output streams for physical properties (flow rate, density, moisture, etc.), PCBs, PCDDs/PCDFs, PAHs,

chlorobenzene and chlorophenol, VOCs, 13 trace metals, HCl, O_2, CO_2, CO, SO_2, NO_x, THC, and other selected compounds.

RESULTS

The principal results of the reactor Demonstration are the following:

- Achieved DREs for PCBs 99.9999 percent or greater, while DEs for PCE, a tracer compound, achieved 99.99 percent.
- Formed no dioxins or furans.
- Exceeded MDNR permit limitations only on benzene emissions (73 to 106 μg/dscm).
- Produced minimal HCl and criteria air pollutant emissions.
- Indicated system capacity factor in range varying from 20 percent to 55 percent.

CONCLUSIONS

In general, ELI's reactor system effectively destroys PCB contaminants, reducing them to lighter hydrocarbons. Destruction efficiencies depend on both the gas-phase reduction reactions—which produce the reformed gas—and on the propane/reformed gas-fired boiler—a combustion device. The boiler polishes the reformed gas before release to the atmosphere. Stack emissions generally meet stringent regulatory levels. However, benzene concentrations in the stack gas and scrubber liquor require close monitoring. The reformed gas composition resembles coal-gas fuel. The scrubber liquor may require disposal as a RCRA waste, unless it can be recycled through the system for additional treatment.

Since the TDU did not operate as anticipated, EPA employed the TDU test data to evaluate system proof-of-concept rather than evaluating a fully developed unit. The test data suggest that the TDU achieved desorption efficiencies at the expense of throughput. Inadequate organics desorption indicate that the TDU requires further development. However, the proof-of-concept data were useful in identifying system strengths and deficiencies.

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VITRIFICATION of SUPERFUND SITE SOILS and SLUDGES

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Vitrification of nonnuclear, hazardous waste can offer the advantage of chemically altering the inorganic, hazardous species through their incorporation into the structure of stable glass. This paper will review the development of glass compositions suitable for treating soils contaminated with inorganic waste. Efforts directed toward demonstration of the feasibility of continuously processing a waste stream of mixed inorganic and organic waste into one of those stable compositions will also be discussed. Initial cost comparison of such a process and cementitious immobilization indicate that vitrification is cost competitive when the cost of landfilling the reduced volume of glass is included in the analysis.

TCLP results for 10 independent replicates.

	ppm in extract liquid						
No.	As	Cd	Cr	Cu	Pb	Ni	Zn
1	<0.10	<0.01	0.02	0.20	0.10	<0.01	0.29
2	<0.10	<0.01	0.02	0.22	0.10	<0.01	0.21
3	<0.10	<0.01	0.01	0.79	0.10	<0.01	0.71
4	<0.10	<0.01	0.02	0.13	0.10	<0.01	0.26
5	<0.10	<0.01	0.03	0.38	0.20	<0.01	0.34
6	<0.10	<0.01	0.02	0.76	0.10	<0.01	0.25
7	<0.10	<0.01	0.01	0.18	0.10	<0.01	0.20
8	<0.10	<0.01	0.02	0.20	0.10	<0.01	0.24
9	<0.10	<0.01	0.02	0.23	0.10	<0.01	0.21
10	<0.10	<0.01	0.02	0.46	0.20	<0.01	0.22
MEAN	<0.10	<0.01	0.019	0.355	0.130	<0.01	0.293

A student's-t test confirms that all of the regulatory specifications for toxic release are met at the 95% confidence level. In fact, a similar analysis performed at 1/10 the regulatory limit is also passed at the 95% confidence level.

PHOTOTHERMAL DESTRUCTION OF OFF-GAS FROM SVE AND THERMAL DESORPTION TREATMENT PROCESSES

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INTRODUCTION

Soil vapor extraction (SVE) has been proven to be very effective to remove volatile organic compounds (VOCs) and some semi-volatile organic compounds (SVOCs) from contaminated subsurface soil at many sites. Thermal Desorption (TD) is the most adapted technique for the separation of VOCs and SVOCs from the excavated soil(1). The off-gas from these two processes are usually adsorbed on activated carbon or condensed to liquid state. The disposal or treatment of these waste residuals is a tedious and expensive task. The treatments of waste water contaminated with organic compounds using the combination of ultraviolet (UV) irradiation and oxidants such as hydrogen peroxide and/or ozone are used commercially(2). However, the powerful photolysis of organic vapor is still not used for the treatment of VOC air emission. Recently, the U.S. Environmental Protection Agency (EPA) has conducted a study on the photolysis of VOCs from SVE at ambient temperature(3). The results showed that the reactions were slow and failed to mineralize the VOCs. In order to solve the aforementioned problem, we have developed a laboratory scale photothermal destruction unit to conduct the tests on VOCs. Preliminary results have shown good results(4). The increase of light absorption and rate of mineralization of some organic compounds with increasing temperature will be shown and discussed in this paper. An effort will be made to develop a detailed design for a prototype photothermal destruction unit for use in processing the effluent from SVE and TD operations.

METHODOLOGY

Absorption spectra of materials of interest were studied at various temperature using a custom built High Temperature Absorption Spectrophotometer (HTAS) with a flow cell as shown in Figure 1. An inert carrier gas (nitrogen) is used for sample transport to avoid the decomposition or oxidation of the testing material. The length of exposure of the sample to elevated temperature is kept short (typically 1 second) to limit destruction of the sample.

Thermal and photothermal reactions were conducted in a Laboratory Scale-Photothermal Detoxification Unit (LS-PDU) as shown in Figure 2. It is equipped with an irradiation source, a cold trap to collect reaction products and unreacted material, and an analytical system which included a gas - chromatograph and two detectors, mass spectrometer and flame ionization detector (GC/MS/FID). Carbon monoxide (CO) and carbon dioxide (CO_2) were collected in a 1 liter Tedlar bag for analysis. The initial concentration and irradiation source of compounds tested in the experiment are listed in Table 1.

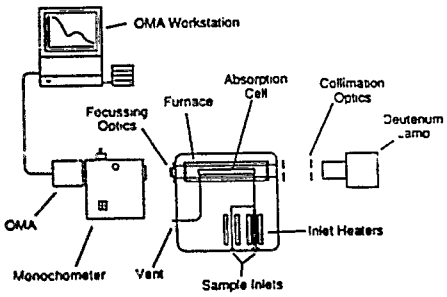

Figure 1.
High Temperature Absorption Spectrophotometer (HTAS)

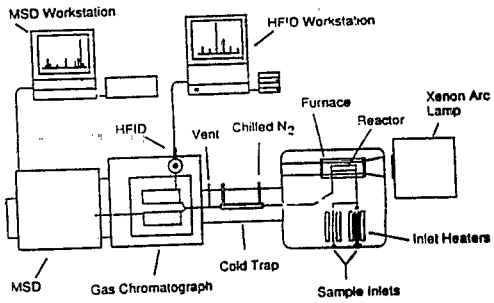

Figure 2.
Laboratory Scale Photothermal Detoxification Unit (LS-PDU)

TABLE 1. INITIAL CONDITIONS FOR COMPOUNDS EXPOSED FOR 10 SECONDS IN DRY AIR

Compound	Initial Concentration	Irradiation Source
Trichloroethylene (TCE)	2.52×10^{-6} mol/L	18.1 W/cm^2 xenon arc (λ>230 nm)
Dichlorobenzene (DCB)	39.4×10^{-6} mol/L	18.1 W/cm^2 xenon arc (λ>230 nm)
Monochlorobenzene (MCB)	25.9×10^{-6} mol/L	0.883 W/cm^2 pulsed laser (λ=280 nm)

RESULTS

Absorption of UV Radiation

Table 2 and Table 3 show the absorption strengths and the onset absorption wavelength of the materials at various temperatures with an 18.1 W/cm^2 xenon arc (a 883 mW, 280 nm laser was used for MCB experiments). The results show that for each compound, the absorption intensity increased, the onset absorption wavelength shifted to longer wavelength, and the overlap (data not shown) with the radiation increased as the temperature increased.

TABLE 2. INTEGRATED ABSORBILITY (λ>230 nm) RELATIVE TO BENZENE AT 100°C

Temp °C	B	T	E	X	TCE	PCE	DCB	MCB	CCl_4	GAS
100	1.00								.0713	
200	1.28	2.33	2.29	3.13	6.16	18.95	5.33	2.33	.139	3.67
300	1.46	2.59	2.57	3.62	8.47	24.12	7.26	2.89	.246	4.35
400	1.73	2.81	2.97	4.21	10.88	26.34	9.52	3.32	.400	5.05
500	1.94	3.33	3.43	5.46	12.59	30.33	12.88	4.89	.661	5.54
600	2.26	3.77	5.25	7.01	15.50	32.04	16.30	6.47	.975	7.29

TABLE 3. WAVELENGTH (nm) FOR THE ONSET OF ABSORPTION

Temp °C	B	T	E	X	TCE	PCE	DCB	MCB	CCl_4	GAS
100	267				262				249	
200		278	281	285		270	290	285		293
600	288	286	290	303	275	288	310	303	288	298

B:Benzene T:Toluene E:Ethyl Benzene X:m-Xylene TCE:Trichloroethylene PCE:Tetrachloroethylene DCB:1,2-Dichlorobenzene MCB:Monochlorobenzene CCl_4:Carbon Tetrachloride GAS:89 Octane Gasoline

Destruction Efficiencies

Tables 4 - 6 summarize the results of thermal and photothermal destructions of TCE, DCB and MCB at various temperatures. Photothermally a significant portion of each compound was destroyed at 300°C, the lowest temperature for which data is typically generated. The extent of destruction steadily increases with increasing temperatures. Furthermore, these compounds may be photothermally destroyed at temperature far lower than required for thermal destruction. All three compounds had significant destruction at the starting temperature (300°C) photothermally. TCE did not start to react until the temperature reached at 500°C while DCB and MCB did not have significant destruction below 600°C thermally.

TABLE 4. DESTRUCTION OF TCE

Temperature(°C)		300	400	500	550	600	650	700
Thermal	%	0	0	0	21	64	99	100
Photothermal	%	12*	30	57	82	93	100	100

*320°C

TABLE 5. DESTRUCTION OF DCB

Temperature(°C)		300	400	500	600	650	700
Thermal	%	0	0	0	0	32	100
Photothermal	%	29	30	34	53	73	100

TABLE 6. DESTRUCTION OF MCB

Temperature(°C)		300	400	500	600	650	700
Thermal	%	0	3	5	7	11	82
Photothermal	%	30	52	62	75	92	100

Products of Incomplete Conversion (PICs)

Most of the three compounds studied were converted to CO and CO_2. Small amounts of various PICs are listed in Table 7 - 9. Except for carbon tetrachloride (CCl_4) from TCE, the amounts of all other PICs produced from photothermal process were relatively small at 500°C or above. The thermal destruction of MCB produced many hydrocarbons at or above 600°C, while the photothermal process produced only small amounts of oxidized hydrocarbons which almost completely disappeared by 500°C. The figures on the photothermal destruction of CCl_4 and tetrachloroethylene (PCE) at high temperatures are anomalous. At present, no explanation can be offered. Further studies on this are planned.

TABLE 7. PRODUCTS OF INCOMPLETE CONVERSION FROM TCE

	% of Fed TCE					
Temperature(°C)	320	400	500	550	600	650
CCl_4						
Thermal	0.0	0.0	0.0	3.0	14.4	10.7
Photothermal	0.0	1.7	9.8	17.8	18.2	7.8
PCE						
Thermal	0.0	0.0	0.0	0.163	0.308	0.403
Photothermal	0.018	0.095	0.220	0.358	0.323	0.188

TABLE 8. PRODUCTS OF INCOMPLETE CONVERSION FROM DCB

	% of Fed DCB					
Temp(°C)	300	400	500	600	650	675
MCB						
Thermal	0.00	0.00	0.03	0.13	0.74	1.06
Photothermal	0.00	0.17	0.48	0.92	1.01	0.29
2-CP*						
Thermal	0.00	0.00	0.06	0.17	0.48	0.26
Photothermal	0.51	0.66	1.05	1.26	0.46	0.05

*2-Chlorophenol

TABLE 9. PRODUCTS OF INCOMPLETE CONVERSION FROM MCB

	% of Fed MCB							
Temp(°C)	300	400	500	600	650	675	690	700
Benzene								
Thermal	—	—	—	—	0.239	0.735	0.689	0.248
Photothermal	0.312	0.612	0.500	0.564	—	—	—	—
Phenol								
Thermal	—	—	—	0.085	1.54	2.48	1.55	0.172
Photothermal	8.60	6.28	2.68	0.869	—	—	—	—

TABLE 9. PRODUCTS OF INCOMPLETE CONVERSION FROM MCB (Continued)

2-Chlorophenol								
Thermal	—	—	—	0.165	1.33	1.90	1.36	0.327
Photothermal	0.685	0.354	0.102	—	—	—	—	—
Maleic Anhydride								
Thermal	—	—	—	—	—	—	—	—
Photothermal	1.22	2.31	1.71	0.125	—	—	—	—
2(3H)Furanone								
Thermal	—	—	—	—	—	—	—	—
Photothermal	0.447	0.647	0.207	—	—	—	—	—
3-Chlorophenol								
Thermal	—	—	—	0.106	1.49	1.84	1.33	0.284
Photothermal	—	—	—	—	—	—	—	—
1-Butene-3-yne								
Thermal	—	—	—	0.680	1.64	1.43	1.40	0.586
Photothermal	—	—	—	—	—	—	—	—
p-Ethynyltoluene								
Thermal	—	—	—	—	0.102	4.67	0.093	0.081
Photothermal	—	—	—	—	—	—	—	—
2-Methylnaphthalene								
Thermal	—	—	—	—	0.146	2.45	0.136	—
Photothermal	—	—	—	—	—	—	—	—
1-Methylnaphthalene								
Thermal	—	—	—	—	—	1.65	0.130	—
Photothermal	—	—	—	—	—	—	—	—

—: not detectable

Performance Prediction

A mathematical model was used to determine the conditions required to achieve a specific percentage of destruction given the fundamental parameters as measured in the laboratory(4). The results of TCE are shown in Figure 3. The results obtained using this model with 18.1 W/cm^2 radiant energy were very close to our experimental data. The model predicts that 99% of TCE may be destroyed by 500°C using a xenon arc illuminating system delivering 100 W/cm^2 of radiant energy.

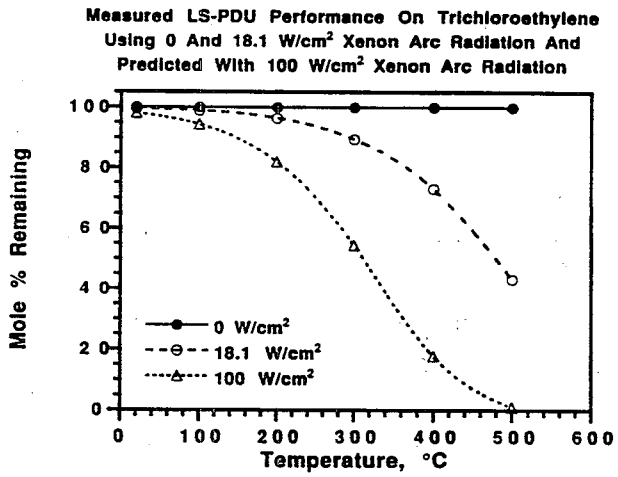

Figure 3.
Destruction of TCE with Xenon Arc Radiation

CONCLUSIONS

The results obtained thus far have demonstrated that various VOCs, including hydrocarbons and chlorinated hydrocarbons, absorb UV radiation at longer wavelength and with increasing efficiency. These effects were greater than were previously anticipated. The photothermal process can destroy VOCs at much lower temperatures than thermal process and can completely mineralize organic vapors that conventional photochemical treatments cannot. After getting more information, a detailed process computer model will be constructed to predict system performance with various reactor vessel configurations, lamp types, and exposure conditions. This will result in the detailed design for a prototype photothermal destruction unit to treat the off-gas from SVE and TD operations.

REFERENCES

1. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Technology Innovation Office: Innovative Treatment Technologies: Semi-Annual Status Report (Third Edition). EPA/540/2-91/001, U.S. Environmental Protection Agency, Washington, DC, 1992. 71pp.

2. Chen, C.T. Assessment of the Applicability of Chemical Oxidation Technologies for the Treatment of Contaminants at Leaking Underground Storage Tank (LUST) Sites. In: W.W. Eckenfelder, A.R. Bowers and J.A. Roth (ed), Chemical Oxidation, Technologies for the Nineties. Vol. 3. Technomic Publishing Company, Inc., Lancaster, PA, 1993. pp 225-248.

3. Blyston, P. Destruction of Organic Contaminants in Air Using Advanced Utraviolet Flashlamps. EPA/540/F-93/501, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1993. 2pp.

4. Chen, C.T., Graham, J.L. and Dellinger, B. Photothermal Detoxification of Air Toxics. Paper presented at 1993 Fall International Symposium of American Flame Research Committee on Impact of the Clean Air Act, Tulsa, Oklahoma. October 18-20, 1993.

POTENTIAL APPLICATIONS AND LIMITATIONS OF TiO_2 PHOTOCATALYTIC OXIDATION FOR THE INACTIVATION OF MICROORGANISMS

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INTRODUCTION

The incorporation of titanium dioxide (TiO_2) as a photocatalyst for the formation of hydroxyl radicals (HO·) in aqueous solutions has prompted the investigation of HO· as a primary oxidant for environmental remediation (1). Minimum HO· concentrations (~10^{-9} molar (M)) generated by irradiating fixed TiO_2 particles (anatase) with ultra violet (UV) light (λ < 400 nanometers (nm)) are much greater than HO· concentrations (<10^{-12} M) generated by other water treatment processes, such as ozonation, direct photolysis of hydrogen peroxide, and radiolysis (2). The use of TiO_2 photocatalytic oxidation for the degradation of anthropogenic organic compounds has been well documented, but there is a dearth of information regarding the practical application of this technology for microbial inactivation. Preliminary investigations support the hypothesis that significant HO· concentrations generated by TiO_2 photocatalysis would serve as an effective biocide because of its high oxidation potential (1.6X and 2.0X that of chlorine and ozone, respectively) and non-selective reactivity (3).

METHODS

A photoreactor was used to treat several 12 liter (L) pure culture and natural water samples. The reactor recirculated samples at 2 L/minute (min) over UV bulbs (λ = 365 nm) bound by a fiberglass mesh impregnated with TiO_2, and sheathed by a stainless steel column (Figure 1). *Escherichia coli* (*E. coli*) was suspended in dechlorinated tap water (2.0 x 10^7 CFU/milliliter (mL)) and recirculated through the reactor.

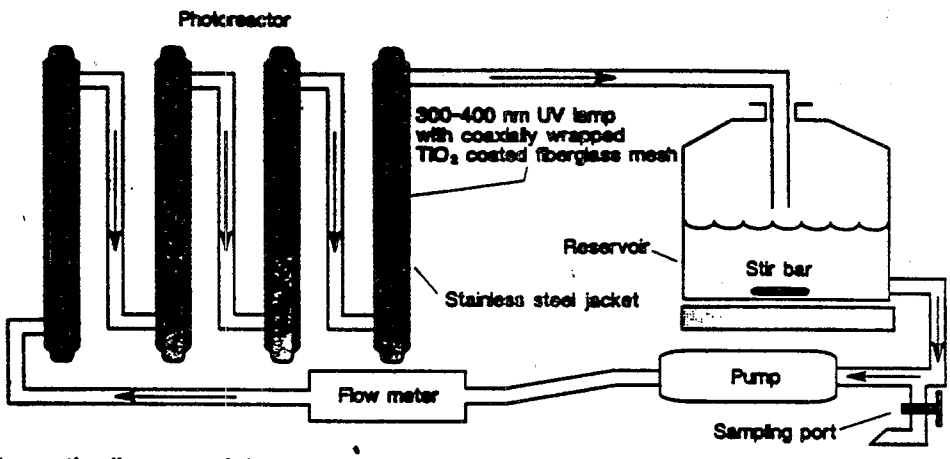

Figure 1. Schematic diagram of the experimental TiO_2 photoreactor showing the flow configuration.

The evaluation of TiO_2 photocatalytic oxidation for microbial inactivation, with regard to potential practical applications, required the conversion of the existing recirculating reactor into a continuous flow (single pass) system. A smaller variable speed centrifugal pump was used to inject sample volumes through the reactor with multiple flow rates. Effluent samples were collected in sterile 50 mL tubes. The new design made it possible to ascertain rates of inactivation with more control and less subjectivity.

RESULTS

Nine minutes of recirculation reduced the viable fraction of a 12 L pure culture E. coli sample $\geq$ 7 orders of magnitude (Table 1). The recirculating reactor performed similarly on the heterotrophic population of a natural surface water (Table 2) when hydrogen peroxide (H_2O_2) was added (6.5 mM at two time points) as an irreversible electron acceptor, used to eliminate HO· scavengers, i.e. detritus. Replicate studies indicated equivalent H_2O_2 concentrations, in the absence of TiO_2 photocatalysis, do not have a significant effect on heterotroph viability.

TABLE 1. INACTIVATION OF *E. coli* OVER UV IRRADIATED TiO_2 IN A RECIRCULATING REACTOR

Sample Description*	*E. coli* Concentration (CFU/mL)
Dechlorinated Tap Water (DTW)	<1
Spiked DTW	2.0×10^7
6-min DTW Recirculation (lamps off)	TNTC†
3-min Exposure	TNTC†
6-min Exposure	2.6×10^2
9-min Exposure	<1
12-min Exposure	<1
30-min Exposure	<1
60-min Exposure	<1

adapted from Ireland, et. al., 1993
*Exposure times are cumulative
†TNTC, too numerous to count

TABLE 2. INACTIVATION OF HETEROTROPHIC BACTERIA OVER UV IRRADIATED TiO_2 IN A RECIRCULATING REACTOR WITH H_2O_2 ADDITION

Sample Description*	Heterotroph Concentration (CFU/mL)
Untreated pond water control	4.8×10^3
Untreated pond water control plus 6.5 mM H_2O_2	2.1×10^3
3-min exposure†	3.6×10^2
6-min exposure	23
9-min exposure with first H_2O_2 addition	9
12-min exposure	14
15-min exposure	4
18-min exposure with second H_2O_2 addition	2
28-min exposure	6
38-min exposure	2

adapted from Ireland, et. al., 1993
*Exposure times are cumulative
†TiO_2 photoactivated

Data generated from the reconfigured reactor design was less impressive than that of the original (Table 3). The continuous flow system required much more contact time/unit volume than the recirculating reactor. Inactivation of similar *E. coli* concentrations required a reduction of sample volume from 12 L to 200 mL. Data generated from the different reactors do not necessarily conflict. They may imply reactor performance is a function of dynamics unique to each system.

TABLE 3. INACTIVATION OF *E. coli* OVER UV IRRADIATED TiO_2 CONTINUOUS FLOW REACTOR

Flow Rate	Influent CFU/mL	Effluent CFU/mL
390 mL/min (no UV)	1.13×10^7	1.02×10^7
390 mL/min	1.13×10^7	TNTC*
155 mL/min	1.13×10^7	TNTC*
40 mL/min	1.13×10^7	<1

*TNTC, too numerous to count

CONCLUSION

The relative poor performance obtained with the current continuous flow system has prompted the evaluation of new continuous flow reactor designs. Increasing the ratio of UV-irradiated TiO_2 particle surface area per unit sample volume has been the crux of design modifications, since HO· does not occur randomly in solution; proximal distance of an HO· to an irradiated TiO_2 particle is infinitesimal. Subsequent studies will focus on the inactivation of samples similar to the aforementioned. As reactor performance improves more resistant organisms, i.e. *Cryptosporidium parvum*, will be employed.

This research was supported in part by an appointment to the Research Participation Program at the Risk Reduction Engineering Laboratory/U.S. Environmental Protection Agency administered by the Oak Ridge Institute for Science and Engineering through an interagency agreement between the U.S. Department of Energy and Environmental Protection Agency.

REFERENCES

1. Haag, W.R. and Yao, C.C.D. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. Environ. Sci. Tech. 26: 1005-1013, 1992.

2. Ireland, J.C. and Valinieks, J. Rapid measurement of aqueous hydroxyl radical concentrations in steady state HO· flux systems. Chemosphere. 25: 383-396, 1992.

3. Ireland, J.C., Klosterman, P., Rice, E.W., and Clark, R.M. Inactivation of *Escherichia coli* by Titanium Dioxide Photocatalytic Oxidation. Appl. Environ. Microbiol. 59(5): 1668-1670, 1993.

SITE DEMONSTRATION OF THE COLLOID POLISHING FILTER METHOD (CPFM)

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INTRODUCTION

A Superfund Innovative Technology Evaluation (SITE) demonstration and evaluation was conducted for the CPFM process developed by Filter Flow Technology Incorporated during the last three weeks of September, 1993. The U.S. Department of Energy (DOE) and the EPA joined together in a cooperative effort to test this technology at the Rocky Flats Plant (RFP) located in Golden, Colorado.

The CPFM technology treated contaminated groundwater collected in an interceptor trench constructed around solar evaporation ponds within RFP. The groundwater contained low levels of radioactivity with a concentration of about 100 picoCuries per liter (pCi/L).

There were three primary objectives in the evaluation of the CPFM technology; 1) to assess the technology's effectiveness in the removal of low level radionuclides from contaminated water, 2) to determine reproducibility of the test system, 3) to determine the costs associated with the operation of the system.

METHODOLOGY

The CPFM technology (figure 1) uses specially designed colloid filter packs in a filter press unit to treat water contaminated with low concentrations of radionuclides or heavy metals.

During the demonstration, radionuclide- or heavy metal contaminated water was pumped from an interceptor trench pumphouse to open-top 500,000 gallon storage tanks, which stored influent for the CPFM system. Treated effluent was routed to a second 500,000 gallon tank. Influent from the storage tanks was pumped into two 200-gallon mixing tanks for pH adjustment and chemical pretreatment. Pretreatment was necessary to adjust water chemistry to the optimum range for contaminant recovery by the filter packs. After pretreatment, the water was gravity fed to a lifter station where it was pumped to a mini-clarifier which removes suspended solids. Settled solids from the bottom of the clarifier were dewatered in a small filter press attached to the clarifier. The solids were then collected and stored in a solids disposal container.

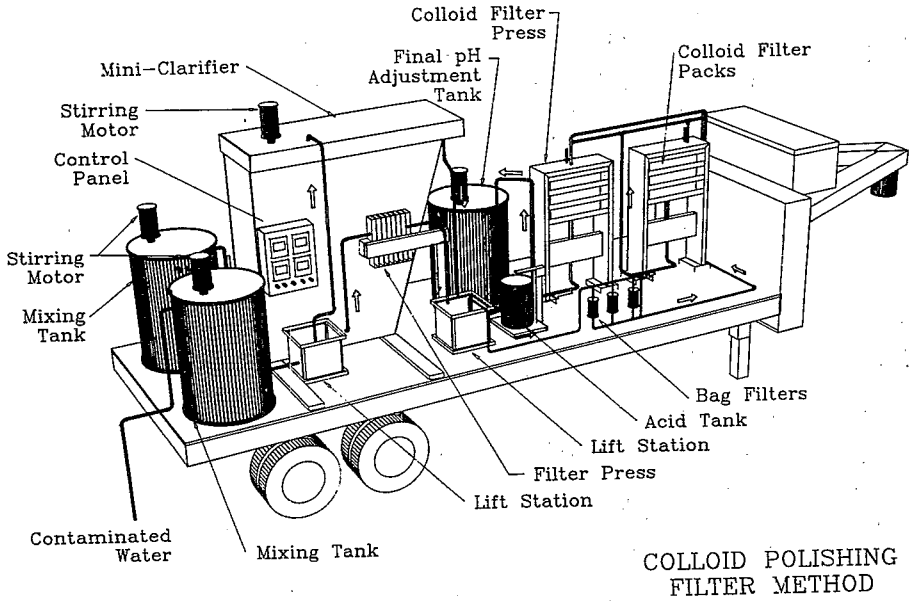

Figure 1. CPFM Schematic.

Effluent from the clarifier was gravity fed to a lift station where it was pumped through a bag filter to remove additional solids greater than 10 microns in size. The system contains three bag filters in parallel so that water may be rerouted if the filters become clogged. Effluent from the bag filters was routed to the colloid filter press units. Each colloid filter press unit was made up of a series of four filter plates containing three colloid filter packs. The colloid filter packs contain an inorganic, insoluble, oxide-based, filter bed material. One filter pack was located between each set of plates within the filter press unit. High pressure was applied to the plates of the colloid filter press unit to promote a tight seal.

The pretreated water was evenly dispersed throughout the filter packs where physical and chemical mechanisms remove contaminants. Chemical complexing with the filter material, adsorption on filter material surfaces, and physical filtration trap contaminants in the filter packs, forming a filter cake that contains about 60 percent solids.

Water passing through the filter packs was then pumped to a final pH adjustment tank. If necessary, effluent from the colloid filter packs may be treated in this tank to reduce the effluent pH before discharge. Once treatment was complete, pressure on the filter plates in the filter press unit was released and the filter packs were removed. The filter cake was then mixed with solids from the mini-clarifier and bag filters and stabilized to meet EPA land disposal restrictions.

The demonstration consisted of three tests. The first test consisted of three runs of 4 hours each, treating about 5 gallons per minute. For the second test, also run for 4 hours at 5 gallons per minute, the influent water was treated with sodium sulfide in the pretreatment tanks to change the oxidation state of the radioactive metals in the water. The third test was a 15-hour run designed to determine the amount of concentration each filter pack is capable of treating.

During the demonstration, samples of untreated influent, pretreated water after passing through the mini-clarifier and bag filters, and treated water that has passed through the filter packs, were collected. Samples were analyzed to evaluate the technology's effectiveness. Adjustment of the influent pH was not required at RFP because the influent water was within the optimum pH range (7.5 to 9.0) for the technology. The pH of the effluent water was monitored in the final pH adjustment tank and was treated to reduce the pH to between pH 9.0 and 7.5 as required by RFP.

PRELIMINARY RESULTS

Bench scale laboratory studies were performed at RFP during the fall of 1991 using feed water spiked with uranium, radium, plutonium, and americium. Results from this study showed promising removal for uranium-234, uranium-238, plutonium and americium with no pretreatment and a pH of 7.6 (Table 1).

TABLE 1. CPFM LABORATORY RESULTS FROM SPIKED FEED WATER

Radiochemistry	Influent (pCi/L)	Effluent (pCi/L)
Gross Alpha	166+15	23+6
Gross Beta	124+8	57+7
Radium-226	13+7	7.4+7
Uranium-234	56+10	.03+.03
Uranium-238	35+6	.01+.03
Plutonium	7+1	.01+.02
Americium	22+4	.01+.01

Similar results were observed when sodium sulfide and sodium bisulfite were added at pH 9.0. Sodium sulfide acts as a reducing agent which decreases the solubility of metals in solution. Sodium bisulfide was added to alter oxidation states from +6 to +4. No differences were observed in metals removal when changing the valence state.

CONCLUSIONS

Key findings from the full scale field demonstration, including complete analytical results and economic analysis, will be presented.

CONTROLLING COPPER, LEAD AND IRON IN SMALL SYSTEMS

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INTRODUCTION

The U.S. Environmental Protection Agency (USEPA) promulgated National Primary Drinking Water Regulations for lead and copper on June 7, 1991.[1] The Lead and Copper Rule (LCR), as it is referred to, establishes "action levels" for lead and copper of 0.015 mg/L and 1.3 mg/L, respectively, at the consumer's tap. Water suppliers that fail to meet either action level are required to employ corrosion control measures to reduce metal levels. Corrosion control treatment strategies include: pH/alkalinity adjustment, silicate addition, orthophosphate addition, and blended (orth- and poly-phosphate combination) phosphate addition.

Determination of an optimum corrosion control strategy can be made through detailed pilot- and bench-scale studies such as pipe loop studies or desk-top evaluations which incorporate the source water quality and current knowledge of lead and copper solubility. Large (>50,000 persons served) and some medium (3,301-50,000) sized water utilities will likely be required to conduct pilot- or bench-scale studies. However, the majority of medium and small (<3,301) sized systems will simply implement some form of treatment due to lack of financial resources and technical knowledge.

Selecting the appropriate corrosion control treatment technique is dependent upon a variety of water quality parameters such as pH, dissolved inorganic carbonate (DIC), and alkalinity, as well as the source(s) of lead and copper (e.g. lead service lines, lead-based solder, brass, or copper pipe). Secondary impacts of corrosion control treatment such as disinfection effectiveness, turbidity, "red water" complaints, and conflicts with other drinking water regulations must also be considered when choosing a strategy. Further, chemical availability, safety issues, personnel, space, and cost are issues to consider when choosing a control strategy.

A concern faced by many utilities is the issue of simultaneous control of lead and/or copper corrosion and "red" and "black" water complaints resulting from iron and manganese in the source water or cast iron lines in the distribution system. Iron and manganese can easily be removed from groundwater by oxidation and filtration processes. However, many of the small and medium sized systems with iron and manganese problems may find construction, material, and sludge disposal costs associated with these treatments costly and may lack the staff to operate and maintain such a facility. These utilities will be faced with finding a simple, economical treatment alternative. Many utilities have alleviated the aesthetic problems by adding either polyphosphates or silicates, to sequester iron and manganese.

A major conflict may arise at utilities that sequester iron and manganese with respect to meeting the LCR. The sequestering ability of these chemicals generally performs best at pH values < 7[2,3,4] which are considered to increase lead and copper solubility[5,6]. In addition, the metal-complexing abilities of these chemicals may result in elevated lead and copper levels. Water utilities unable to construct iron and manganese removal facilities must struggle with finding the appropriate set of water quality conditions and chemical dosages to enable them to continue using the sequestering agents while meeting the requirements of LCR.

The first objective of this paper is to provide a fundamental understanding of the chemistry and chemical conditions which polyphosphate- and silicate-based chemicals may be used to simultaneously address

sequestration of iron and manganese, and reduce lead and copper solubility. The paper discusses the rationale for choosing a treatment, silicate addition, for a medium sized utility in Massachusetts attempting to simultaneously control lead and copper and sequestration of iron. This paper briefly describes the system and baseline monitoring data thus far collected. Unfortunately, at the time of the manuscript preparation, treatment results were not yet available. The basis for this study is an ongoing USEPA cooperative agreement through the New England Water Works Association.

BACKGROUND

The dominant use of sodium silicates in water treatment is to sequester iron and manganese, to reduce consumer complaints on these metals. Sodium silicate solution, is a proportioned mixture of silica and sodium oxide. Sodium oxide causes a specific pH increase for a target dosage of silica. When sodium silicate is introduced into solution and dissolved, silica will initially be in a polymeric form. After a short period of time (15-30 min), the polymeric species likely reverts to a monomeric or polymeric form with shorter chain length. The reversion most likely depends on temperature, pH and ionic strength.

Unlike polyphosphates that react with the non-oxidized form of iron and manganese, silicates react with the oxidized form of these metals through a colloidal dispersion mechanism. For the sequestering process to be effective, chlorine must be injected a few seconds ahead of the silicate[2]. The chlorine promotes rapid oxidation of the iron which forms an iron colloid. Dissolved silica species prevent the growth of the iron colloids. PH values of 7.8 - 8.0 and silica levels of 10 - 12 mg SiO_2/L provided effective sequestering of 2 mg/L of iron. When the calcium content is negligible (<5 mg Ca/L), higher pH values tend to promote more effective sequestering. However, as the calcium concentration increases the optimum pH for sequestering decreases. Higher silica dosages can be used to overcome the negative effects of calcium.

Manganese sequestering with silicate is more sensitive to pH shifts than iron. As pH increases over the range of 7 to 8, the effectiveness is significantly reduced. Overall, sodium silicate is less effective in sequestering manganese than it is for iron.

Historically, silicates have been used to control corrosion of hot water systems[7,8]. The effectiveness of silicate for this purpose depends on pH and the ionic character of the water (e.g. calcium, magnesium, sulfate and chlorides). Outside of this use, very little data exists on how silicates perform in reducing lead and copper levels in distribution systems.

Unfortunately, there has been a lack of research on the ability of silicate to sequester iron and manganese above pH 8.0. At the present time, the ability of silica to control lead and copper based corrosion is unknown. As a consequence, utilities using or considering use of sodium silicate should rely on the better documented benefits of the pH increase that results from the application of sodium silicate.

Polyphosphates can be used to sequester iron and manganese under proper water conditions.[2,9] Polyphosphates revert (breakdown) over time to orthophosphate, which may under the appropriate water quality conditions reduce lead corrosion. Polyphosphates are simple to use, requiring as little as a chemical storage tank and chemical feed pump. They may be added to existing systems with little effort and change.

Polyphosphate products are commercially available in a wide variety of formulations. Specific examples include sodium tripolyphosphate ($Na_5P_3O_{10}$) and sodium pyrophosphate ($Na_4P_2O_7$). More complicated are the glassy polyphosphates which are also commonly referred to as "metaphosphates" or "hexametaphosphates". The composition of glassy phosphates is not clear and their structure is not clearly ordered. Glassy phosphates are produced by heating soda ash or caustic and phosphoric acid which then is allowed to cool and crystalize into a "glassy" plate which is crushed. Amorphous mixtures of long chain polyphosphates can be formed by differing the heating and crystallization conditions.[10] Bimetallic polyphosphates include zinc in the chemical formulation, variety of bimetallic polyphosphates are available with

varying zinc to phosphate ratios, solubilities and inhibitor and sequestering capabilities. Zinc tends to slow the retention rate and limit the dissolution of the polyphosphate, and is thought by some to play a role in corrosion inhibition.[11]

When added to water, polyphosphate revert, breakdown, or hydrolyze with time into mixtures of shorter chain polyphosphates and the orthophosphate ion (PO_4^{3-}). The rate of reversion varies with polyphosphate chemical, water temperature, pH, and other ions such as calcium. Lowering the pH increases the rate of reversion while increasing the effectiveness to sequester iron and manganese. Higher temperature and calcium concentration also increase the rate of reversion. A consideration, particularly to utilities with long retention times in the distribution system, is the issue of reversion and the loss of sequestering effectiveness at distant sites from the treatment facility. The original chemical may revert to a form that is less likely to sequester a desired metal at a distant site, resulting in aesthetic complaints from consumers. Further, the experience of one researcher suggests utilities should consult with the polyphosphate manufacturer concerning storage time and chemical deterioration.[2]

Robinson et al.[2] pointed out that the degree of sequestration of iron and manganese depends on chemical, pH, and calcium concentration. These authors found that turbidity may increase when phosphates are used in waters containing calcium as a result of the precipitation of calcium orthophosphate. A trade-off between turbidity and color formation existed, and that by fine tuning polyphosphate dosage optimal conditions could be achieved. Best iron sequestration was found at lower pH's (i.e., 6.0-8.0), however, as the pH increased the solubility of calcium orthophosphate increased. It was also suggested that polyphosphate hydrolysis and colloidal particle charge change with pH.

The ability or strength of polyphosphates to sequester metals varies with chemical due to the structural chemistry of the different polyphosphate ions in solution.[11] Secondly, the preference to sequester one metal over another varies with polyphosphate. For example, one chemical may sequester calcium better than iron or manganese while another may sequester iron better than calcium or manganese.

Calcium complexation by polyphosphates inhibits the precipitation of calcium carbonate, although the inhibition may also probably involve absorption of the polyphosphate to the crystal face of calcium carbonate, inhibiting its growth (i.e., crystal poisoning).[12,13].

Polyphosphate must be introduced to the water prior to oxidation of the iron and manganese by oxidizing agents such as chlorine or oxygen. Polyphosphates, unlike silicates, sequester by preventing iron and manganese to be oxidized.[2] Strong oxidizing agents in the water system (i.e. laundry bleach) could overpower the sequestering capabilities of polyphosphates and oxidize bound iron or manganese. If this is a concern, polyphosphate dosage adjustment may be required.

The issue of using polyphosphates for lead and copper control is a controversial one. Holm and Schock[11] point out concerns and risks for the potential of increase lead solubility in drinking water systems. Other researchers have observed similar findings under field conditions.[14,15,16,17] Further, utilities treating for iron and manganese are typically operating at low pH conditions as suggested for optimization, but the low pH can adversely affect lead and copper solubility in the system. The reversion of polyphosphates to orthophosphate may be beneficial towards lowering lead solubility. Orthophosphate used under the proper pH conditions has been demonstrated to inhibit lead corrosion. "Blended" phosphates are chemical manufacturers answer to controlling iron and manganese complaints and controlling lead corrosion with the same chemical. Blends consist of a mixture of polyphosphate (for Fe and Mn control) and orthophosphate for lead control. Unfortunately, little data is in the literature that sufficiently identifies experiences with blends and describe chemicals and dosages for particular conditions.

Due to the proprietary nature of polyphosphates and blended phosphate chemicals, little information concerning the composition, solubility, reversion rate, affinity for sequestration, temperature and pH effects,

and effects on lead and copper solubility are described in the peer reviewed literature. This of course, requires utilities to rely on manufacturers for technical support and guidance. As has been pointed out, the use of polyphosphates effectively is a function of many variables and is site specific. Issues to be considered include: raw water quality (pH, temperature, calcium), iron and manganese, chlorination, reversion rate, copper and lead corrosion. Interpretation of previous experiences with polyphosphates is difficult do to the diversity of the issues mentioned.

METHODOLOGY

A medium sized (serving 7600 people) utility in Massachusetts receives it's drinking water from five gravel wells, each with a pump station. Two of the five wells contain elevated levels of iron (as high as 2 mg/L) and manganese (0.02 to 0.23 mg/L). A polyphosphate chemical has been added to those wells to prevent red and black water complaints. The remaining three wells are untreated. All sources have a pH of 5.9-6.2 and a DIC of approximately 13 mg C/L. The community has exceeded both the lead and copper action levels (90th percentile values of 0.077 and 5.87 mg/L of lead and copper, respectively).

The city has identified 14 sites to perform lead and copper monitoring over the duration of the study. Three rounds of sampling for lead and copper (and a variety of other important water quality parameters) along with 2 rounds of sampling for the LCR have been used to establish a consistent baseline. Currently, the system is completing installation of chemical feed units at the well sites.

Early on, thought was given to using a "blended" phosphate for simultaneous control of lead, copper, iron, and manganese. Theoretically, a proper blend could sequester iron and manganese via the polyphosphate portion and reduce lead via phosphate presence. The pH would need to be raised for optimal lead reduction to approximately 7.3-7.6, which would likely benefit copper reduction, but, reduce sequestering capability. Several problems exist, however. First, the blend used would have to be well-defined in that polyphosphate type, reversion rates, ratio of poly- to orthophosphate could be identified. Due to the proprietary nature of these chemicals, no manufacturer would provide this information. Specific compositions of blended phosphate compounds vary quite dramatically from manufacturer to manufacturer. Therefore, data generated from this study would be specific to the particular chemical used and could not be extrapolated to other polyphosphate compounds. Secondly, we would be operating at a threshold between minimum iron and manganese sequestration and optimal lead control, which results were somewhat uncertain. And, finally, the utility would need to add two chemicals; a blended phosphate and a pH adjustment chemical.

Because of the above reasons, sodium silicate was chosen to be used at this community. As mentioned, sodium silicate contains silica for control of iron and manganese and sodium oxide for pH adjustment. Sodium silicate requires only one feed system and different ratios of SiO_2 to Na_2O solutions are available. Lower ratios result in products that are more basic, resulting in greater pH increase benefit. The pH range that silicates control red water, extends to at least pH 8.0. Therefore, higher pH water values could be achieved for lead and copper control without jeopardizing iron sequestration. Currently a cost/benefit analysis is being conducted to identify which chemical ratio will be used. The system will aim to add 20 mg SiO_2/L and a pH of 7.5.

CONCLUSION

A medium sized utility in Massachusetts is combatting the issue of simultaneous control of lead and copper and iron precipitation complaints by customers. The system is limited from the standpoint of monetary resources, personnel, and technical knowledge which are common deficiencies among many small and medium sized utilities in the United States. It has been decided that sodium silicate addition would provide the utility with the best treatment approach. Sodium silicate treatment would be simple, require little attention, and would be relatively inexpensive. Baseline sampling has been concluded at 14 sites in the distribution system and current progress is being made towards installing chemical feed pumps at the wells. Unfortunately at the time of preparation of this manuscript data is not available on the treatment results.

REFERENCES

1. Lead and Copper. Final Rule. *Red. Reg.*, 56:26460 (June 7, 1991).

2. Robinson, R. B., ET AL. Sequestering Methods of Iron and Manganese Treatment. AWWA Res. Fdn., Denver, CO. (1990).

3. Robinson, R.B., Minear, R. A., and Holden, J. M. Effect of Several Ions on Iron Treatment by Sodium Silicate and Hypochlorite. *Journal AWWA*, 79:7:116 (July 1987).

4. Robinson, R.B. and Ronk, S.K. The Treatability of Manganese by Sodium Silicate and Chlorine. *Journal AWWA*, 79:11:64 (Nov. 1987).

5. Schock, M.R. Understanding Corrosion Control Strategies for Lead. *Journal AWWA*, 81(7):88 (1980).

6. Schock, M.R. and Gardels, M.C. Plumbosolvency Reduction by High pH and Low Carbonate-Solubility Relationships, *Journal AWWA*, 75(2):87 (1983).

7. Falcone, J.S., ed. Soluble Silicates, ACS Symposium Series 194, American Chemical Society, Washington, D.C., 1982.

8. Lane, et al. The Effect of pH on Silicate Treatment of Hot Water in Galvanized Piping. *Journal AWWA* (August 1977).

9. Klueh, K. and Robinson, R. B. Sequestration of Iron in Groundwater by Polyphosphates. *Journal of the Environmental Engineer Div., ASCE,* 114:5:1192 (Oct., 1988).

10. AWWA Research Foundation/DVGW Forschungsstele. Internal Corrosion of Water Distribution Systems. AWWARF Coop. Res. Rept. AWWARSF, Denver, CO. (1985).

11. Holm, T.R. & Schock, M.R. Potential Effects of Polyphosphate Products on Lead Solubility in Plumbing Systems. *Journal AWWA*, 7:76:82 (July, 1991).

12. Berner, R.A. Rate of Concretion Growth. *Geochim. Cosmochim. Acta,* 32:477 (1968).

13. Berner, R.A. and, Morse, J. W. Dissolution Kinetics of Calcium Carbonate in Sea Water. IV. Theory of Calcite Dissolution. *American Journal of Science*, 274-108 (1974).

14. Hatch, G.B. Inhibition of Lead Corrosion With Sodium Hexametaphosphate. *Journal AWWA,* 337:7:1179 (July, 1941).

15. Baily, T.L. Corrosion Control Experiences at Durham, N.C. Proc. 1982 WQTC, Nashville, Tenn., Dec. 5-8.

16. Sheiham, I. & Jackson, P.J. The Scientific Basis for Control of Lead in Drinking Water by Water Treatment. *Journal Inst. Water Engineers and Scientists*, 35:6:491 (Nov. 1981).

17. Neff, C.H., ET AL. Relationship Between Water Quality and Corrosion of Plumbing Materials in Buildings. Final Report CR8566-02. EPA/600/S2-87/036, Cincinnati, OH (1987).

ULTRAFILTRATION MEMBRANE RESEARCH FOR SMALL DRINKING WATER SYSTEMS

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Both small community and non-community drinking water systems (serving less than 3,300 people) have and will continue to have difficulty complying with the ever increasing number of regulated contaminants. Currently, it is estimated there will be nearly 100,000 violations of the Safe Drinking Water Act annually. Approximately half of these are for Maximum Contaminant Level (MCL) violations. Of these, the majority are microbiological violations by the small systems. The Surface Water Treatment Rule along with the future Ground Water Disinfection Rule and Disinfection/Disinfection By-Products Rule will especially impact small systems.

The Safe Drinking Water Act (SDWA) and it Amendments mandate the regulations of all public water systems that have 15 or more service connections or serve at least 25 people for at least 60 days each year. These public water supplies include community and non-community systems such as schools, factories, and hospitals that have their own water supplies but usually exclude noncommunity systems that cater to transitory customers in non-residential areas such as campgrounds, motels, and gas stations.

Of the approximately 200,000 public water systems in the United States, about 30 percent are community water systems which serve primarily residential areas and 90 percent of the population. Of the 59,266 community water systems, which serve about 232 million people, 51,682 were classified as "small" or "very small." These systems served populations of fewer than 3,300 people, with a total population served of about 25 million people (Table 1).

Small systems are the most frequent violators of federal regulations and accounted for almost 88 percent of the violations posted in 1991. Microbiological violations accounted for the vast majority of the cases with failure to monitor and report (M/R) exceeding violations of the SDWA Maximum Contaminant Levels (MCLs).

Membrane technology is being considered for designation as BAT for the pending regulations and in order to develop cost and performance information the U.S. Environmental Protection Agency Drinking Water Research Division in Cincinnati, Ohio has-developed a Small Systems Research Program. The research incorporates both in-house and field investigations.

TABLE 1. COMMUNITY WATER SYSTEMS BY SIZE DISTRIBUTION

System Size (Population Served)	No. of CWS*	Percent of CWS	Population Served (Million)	Percent Population Served
Very small < 500	37,226	63	5.7	2
Small 501 - 3,300	14,456	24	19.8	9
Medium 3,301 - 10,000	4,238	7	24.4	10
Large 10,001 - 100,000	3,034	5	83.5	36
Very large > 100,000	312	1	99.2	43
National total	59,266	100	232.6	100

*Community water systems

Two field projects that have installed UF membrane package plants in diverse communities are presented in this report. The first being in the hills of West Virginia treating water from a collapsed mine shaft that serves approximately 100 people. The second community is located on the Chemehuevi Indian Lands on the western shore of Lake Havasu in the California desert. This community serves approximately 500 people utilizing the impounded Colorado River as the source of supply. During the hot summer months there is a tremendous amount of recreational activity on the lake and there have been reported cases of *Giardiasis* in neighboring communities.

UF ADVANTAGES FOR SMALL SYSTEMS

Ultrafiltration (UF) is an effective means of removing particulates and dissolved polymers from water sources as diverse as sea, river and groundwater. UF membranes fall in between the range of reverse osmosis (RO) and microfiltration (MF). Since UF cartridges operate in a cross-flow mode,there are similarities between UF and RO systems.

A major reason for small system use is that UF systems operate at pressures up to 120 psi, offering much lower pressures than RO systems which operate at hundreds of psi. Second. UF cartridges permeate at rates approaching 30 GSFD (gallons per square foot of membrane per day), in contrast to RO membranes which flux in the order of 15 GSFD-rejecting salts and other low molecular weight components that need not be removed from municipal water. Third, UF systems produce much more water at lower operating pressures than RO systems, and therefore, both the capital and operating costs for UF systems are significantly less.

Other benefits of using ultrafiltration include:

- Ultrafiltration eliminates the need for chemical coagulants or filter aids.
- Ultrafiltration produces higher quality filtrate than using granular media filtration alone. In general, the silt density index of ultrafiltered water approaches zero.
- UF systems can operate at much higher recoveries than RO systems.
- Ultrafiltration does not exhibit solids breakthrough associated with granular media filtration.
- UF cartridges, designed with proper cross-flow velocities and with routine cleanings, can eliminate the bacteria typically found in conventional flow-through filters.
- UF cartridges can be fed high turbidity water without frequent replacements.
- UF membranes can be sanitized with up to 200 PPM of NaOCl.

BUCHANAN, WVA

The Buchanan, WVA system is one of eleven operated by the McDowell County Public Service District (PSD). The Buchanan system serves approximately 100 people requiring about 10,000 gallons over a 24 hour period. The water source is an abandoned coal mine that has collapsed and been sealed off to keep animals out. The raw water quality is very good with low levels of bacteria, turbidity, trace metals, and inorganic contaminants. Previous treatment included super chlorination of sand filtered water. Both pieces of equipment were near collapse and although currently in compliance, produced unpalatable water.

HAVASU LANDING, CALIFORNIA

The Chemehuevi Indian Lands is located on the western shore of Lake Havasu in the California desert. Approximately 87 homes and 400 people are served in one of the two systems being operated by the tribal government. Water usage peaks at three times the average demand during the summer months because of the use of evaporative cooling (swamp coolers) for the homes. Per capita consumption can average 300 gallons per day for several days continuously. Past water treatment consisted of a pressure sand filter followed by chlorination. Because of capacity limitations and equipment design, bacterial violations had been occurring and the system was under a consent decree to improve water quality. Raw water quality experienced spikes in TDS and Giardiasis had been reported in nearby communities. Algal blooms also occur in the late summer.

A package plant similar to the one in Buchanan, WVA was installed with a 40 gpm capacity. Pre-treatment consisted of the rehabilitated sand filter (without chemical additions) and a cartridge filter prior to the UF bag filter to prolong the UF membrane operation by removing the potentially high TDS levels. A concrete pad and roof were installed by the system technicians to house the package plant.

RESULTS

BUCHANAN, WVA

Over the first 15 months of system operation at Buchanan, WV some informative results have been documented. The UF plant cycles on and off in operation based on sensors in the 3,000 gallon storage tank. Daily system operation ranged from about 9.5 to 17 hours/day. In order to maintain a consistent permeate flow of approximately 10 gpm during operation, the transmembrane pressure (TMP) was periodically increased in response to membrane fouling. The system was operated with adjustments to TMP until the inlet high pressure gauge indicated a membrane cleaning was needed. Also, prefilter inlet pressure was tracked to provide an indication of when bag filter replacement was necessary. Generally, bag filters were replaced when membrane cleaning was performed, and at some additional non-cleaning times. Membrane flux was consistently maintained at 20 gsfd or above.

Initial data indicates that the UF system is operating according to specifications. Preliminary water quality data for the UF system show good reductions in particles and bacteria. Little TOC reduction is observed as expected for a 10,000 MWCO membrane. During this sampling period, 1.40 PPM sodium hypochlorite was injected into the recirculation loop prior to the membrane vessel. There are small increases in TOX, THMs, HAAs, and HANs. Preliminary samples indicate some aldehydes in the raw water with possible biodegradation and/or chemical reaction with chlorine occurring. An increase in AOC is observed with a possible link to the aldehydes and chlorine addition. The inorganic chemical parameters are not removed by the UF system as expected. Some iron and manganese precipitation onto the membranes occurred requiring an acid wash. Hence, chlorine addition was moved from the recirculation loop (pre-membrane) to post-membranes after about 1520 production hours.

HAVASU LANDING, CA

Since December 1992 when the ultrafiltration membrane package plant became operational there have been a variety of modifications to the operation, treatment train, and frequency of maintenance. Because of these many changes and institutional problems, there has been little opportunity to fully evaluate and challenge the package plant. Initial emphasis was on productivity and becoming familiar with the operation of the system. During the first three weeks, the system operated well with only one prefilter change being necessary. However, the system was not cleaned throughout the first month and productivity declined considerably. Membrane cleaning occurred at irregular intervals over the next few months with productivity only partially returning after cleaning. By April it appeared that the membrane was severely but not irreversibly fouled. It was decided to clean the membrane every two weeks to try to return the membrane's productivity and move the point of chlorination to the sand filter to prevent algal growth in the system. It was also recommended that the sand be replaced in the roughing filter since it was very old. It was also recommended that a larger water heater be installed in order that warm water be available for the entire cleaning. Throughout the summer months, cleaning intervals remained erratic although the sand was eventually replaced in the roughing filter.

Monthly water sampling began in February 1993 for a wide variety of parameters. The parameters of most interest included total coliforms, fecal coliforms, turbidity, TOC, and disinfection by-products. In most cases, it is evident that the finished water was not in compliance given the few total coliforms found in the package plant permeate. The membrane nominal pore size is .005 microns and should remove bacteria. Whether these occurrences are because of lack of membrane integrity, sampling error, or biological grow-through of the membrane is difficult to determine. Routine sanitizing of the short runs of PVC pipe at the sampling port is being implemented to address one contamination possibility. Given the low intermittent total coliform levels, post-chlorination of the permeate water will provide another safety barrier and produce finished water in compliance with the Total Coliform Rule.

Finished water turbidity values were with only one exception very good. Even values as low as 0.2 NTU required by the State of California are routinely attainable by the package plant. TTHM levels were very low (< 10 ug/L) even during periods of pre-chlorination. Other by-products were negligible. As expected, the package plant had little effect on the trace metals or inorganic parameters. Raw water levels for these parameters were not a concern nor did they pose any serious constraints to the operation of the package plant other than the awareness of some scale formation from hardness and the algal blooms already mentioned.

COST

The Buchanan, WVA Plant cost $25,000 to purchase. O&M costs have been estimated to be approximately 10 dollars per household per month. Nearly half of this O&M expense is for an operator to visit the plant daily for inspection. Retrofitting the system for remote monitoring will reduce O&M costs considerably. The Havasu Landing plant cost approximately $65,000. O&M costs have not been developed yet because of the productivity problems encountered to-date.

POINT OF USE TREATMENT FOR ARSENIC REMOVAL

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This study was conducted to determine whether point-of-use (POU) reverse osmosis (RO) units could satisfactorily function in lieu of central treatment. The POU units were to remove arsenic and fluoride from the drinking water supply at San Ysidro, NM. POU treatment was evaluated for removal efficiency, cost, and management effectiveness.

Seventy-eight under-the-sink model RO units were installed in private homes. Of the 78 units installed, 72 units were monitored for about 18 months to evaluate operational and maintenance data for POU treatment.

INTRODUCTION

The Village of San Ysidro is a small rural community of approximately 200 people located in the north central part of the State of New Mexico approximately 45 miles (72 km) north of Albuquerque. The Village was having problems meeting water demands and was also out of compliance with the Drinking Water Regulations for arsenic and fluoride. Feasibility studies were performed to determine whether economical improvements to the system could be recommended (improvements that would solve both San Ysidro's water quantity and quality inadequacies).

The Village has had a long history of water supply problems including low water pressure and at times, no water at all. They also had water quality problems including taste, color, clarity, and odor in addition to arsenic and fluoride contamination and sporadic coliform violations. The water supply source is an infiltration gallery that produces an average of 27,000 gpd in the winter and 36,000 gpd in the summer from the groundwater. The Village uses an average of 30,000 gpd, which equates to about 150 gpd per person. This consumption rate pushed the production limits of the gallery.

Central treatment of the entire water supply was not considered feasible for many reasons. First, a disposal problem exists with both the arsenic contaminated wastes from activated alumina regeneration and the reject brine from an RO system. Second, the capital costs and the operation and maintenance costs of central treatment were determined to be higher than POU treatment. And, lastly, central treatment was considered too complicated to be efficiently operated by a community the size of San Ysidro. The solution in this case was determined to be POU treatment with RO units.

METHODOLOGY

A notification letter was sent to each water customer, and a public hearing was held on December 18, 1985. At this meeting, the cooperative agreement between the Village and the EPA was brought before the villagers to explain the water quality problem and to discuss the procedures needed to have the RO POU devices installed, maintained, and tested during the study period. The Village passed an ordinance requiring the installation of an RO system in each water customer's home if the home had indoor plumbing. The ordinance was deemed necessary because POU treatment could not

be considered a viable alternative to central treatment for a public water system unless the utility furnished safe drinking water to each water customer. Each water customer also had to sign a permission form to allow the Village to install the unit in their home and to allow access to the unit for testing and maintenance. The permission form was necessary because an ordinance could not give the Village the authority to enter a person's house (only an individual can grant permission to the Village to enter his home).

A Request for Proposal was prepared in which contractors were asked to prepare competitive bid proposals for furnishing approximately 80 RO units. The bid proposals was to include installation and 14 months of unit maintenance.

The RO units were required to be under-the-sink models capable of producing a minimum of 5 gallons of drinking water per day with a storage capacity of 3 gallons. The system pressure range was given as 40 to 60 psi maximum, with a minimum pressure of 20 psi.

A contract was given to both install and maintain the RO unit. Within the first 4 months of the project, 73 RO units were installed, and 5 more were added by the end of the project period. Of the 78 units installed, however, only 72 units were actually available for testing on a regular basis. At three homes, totalizing meters were installed on the inlet line to the RO units to measure the amount of water used by the system.

RESULTS

The RO units were operated and monitored for an 18 month period. Water samples were scheduled to be collected every other month for arsenic and fluoride analyses. In addition,the units were to be samples every 4 to 6 month for chloride, iron,and manganese. Because of various restrictions, only 40 units were analyzed for total coliforms. Each month, an average of 31 units were sampled for arsenic and fluoride; of these, 15 were also sampled for chloride, iron,and manganese and 10 for total coliforms.

The average water use by the RO systems recorded at the three homes with totalizing meters varied from 8.5 to 17.0 gpd. Water use varied because of the size of the families and their use of the RO-treated water. Product water production (recovery) by the RO system depends on inlet water pressure and TDS, but ranges from 20% to 30% of the total flow in the unit at 50 psi and less than 1,500 ppm TDS.

The RO units effectively removed arsenic and fluoride from the water. The RO units also effectively removed chloride, iron, manganese, and TDS. Because of the high costs of arsenic and fluoride analyses, conductivity measurements were evaluated as a substitute for arsenic and fluoride tests. An analysis of the arsenic, fluoride and conductivity data showed a rule of thumb could be established whereby a conductivity measurement of less than 600 micromohs/cm would maintain less than 0.03 mg/L of arsenic and less than 1.0 mg/L of fluoride.

CONCLUSIONS

The following conclusions were drawn as a result of the San Ysidro study.

POU treatment of drinking water is an effective, economical, reliable, and viable alternative to central treatment in a small community like San Ysidro to remove arsenic as well as other contaminants.

Adopting a POU treatment system in a small community requires more care than does a central treatment system relative to time-keeping to monitor the individual systems.

POU systems require special consideration from regulatory agencies to determine appropriate methods for record keeping, monitoring, and testing frequencies that may differ from existing regulations.

The RO units with polyamide membranes installed in San Ysidro resulted in the following removal percentages, bringing all of the contaminant levels well below the MCL's: arsenic (total) - 86%; fluoride - 87%; TDS - 88%; chloride - 84%; iron - 97%; and manganese - 87%.

The cost to the customer of POU treatment per month ($7) in San Ysidro is less than half of the estimated cost of central treatment ($30 to $40 per month). The cost per gallon of treated water, however, is more than three times that of central treatment, since central treatment treats the entire water supply and the POU device treats a small fraction of the supply.

THE EFFECTIVENESS OF SORBENTS FOR SOLID-BED METAL CAPTURE IN AN INCINERATOR: SCREENING TESTS AT THE INCINERATION RESEARCH FACILITY

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INTRODUCTION

Given the concern over the emission of hazardous constituent trace metals from incinerators, there is currently considerable interest in the potential use of mineral-based sorbents for capturing and retaining those metals in the incinerator "ash" discharges (fly ash and bottom ash).

Most of the research completed to date has focussed on quantifying the effectiveness of various proposed sorbents for capturing vaporized metals from the flue gas. In such applications, it is theorized that vaporized metals will react with the sorbent particles at elevated incinerator temperatures or heterogeneously condense onto the sorbents as the flue gas cools. In the absence of available condensation sites, vaporized metals will primarily undergo homogeneous condensation, forming a fine fume. Thus, the goal with flue-gas sorbents is to make particles available with which the metals can react or upon which the metals can condense. Metals bound to larger sorbent particles will be more effectively collected by air pollution control systems (APCSs) than metals presented as a fine fume. Studies completed to date suggest that chemical reaction between the metal and the sorbent dominates over physical adsorption, offering the additional advantage of reduced potential for metal leaching from collected particulate.

Other researchers have studied the incorporation of sorbents into the solid feed. This approach seeks to capture and bind the metals in the incinerator bottom ash, preventing them from exiting with the combustion gases. Research completed to date suggests that for this approach to be effective, the metal should become volatile in the incinerator environment and chemically react with the sorbent material.

The subject test program was designed to further investigate this second approach by screening several minerals for their suitability as sorbent materials for capturing metals in the solid bed and preventing their release to the flue gas. In addition to capturing the metals, an ideal sorbent would retain them in the ash when disposed, so that extraction of the ash by the toxicity characteristic leaching procedure (TCLP) would yield a leachate with metals concentrations below respective regulatory levels. Accordingly, the objective of this screening program was to evaluate several candidate sorbents with respect to: (1) the degree to which they facilitate retention of trace

metals in the ash/solid bed discharged from an incinerator; and (2) the degree to which they retain trace metals in the solid bed when subjected to TCLP extraction.(1)

METHODOLOGY

Test Equipment

The screening tests comprising this program were conducted in the bench-scale thermal treatability unit (TTU) at the U.S. EPA Incineration Research Facility (IRF). The TTU is a small commercial pathological incinerator that has been modified to allow for continuous test material feed and treated material (e.g., ash) removal; for variable and controlled treatment temperatures; and for expanded process operation monitoring (Figure 1).

The combustor portion of the TTU consists of three chambers. The charge chamber is designed to accept the solid material feed stream and corresponds to the primary combustion chamber (or kiln portion) of a waste incinerator. The retention chamber, which directly follows the charge chamber, is designed to effect further organic constituent destruction and corresponds to the secondary combustion chamber (or afterburner) of a waste incinerator. The breaching chamber serves as a second-stage afterburner. Volumes of the charge chamber, retention chamber, and breaching chamber are 0.82 m^3 (29 ft^3), 0.67 m^3 (23.5 ft^3), and 0.10 m^3 (3.5 ft^3), respectively. Each of the three chambers is fired with natural-gas-fueled burners.

A feed system transports quartz trays containing the test material through the charge chamber using a variable-speed chain-drive mechanism. The system can accommodate a number of different tray sizes; those used for the subject tests were 18.5 cm (7.3 in) long by 8.5 cm (3.3 in) wide by 4 cm (1.6 in) deep, and were capable of holding up to 1 kg (2.2 lb) of test material.

Test Program

The test program consisted of 50 tests, including two duplicates of one test condition. Test variables were sorbent material type, solid bed temperature, feed chlorine content, and metal form in the feed.

Six sorbents were evaluated. Four of the six (diatomaceous earth, kaolinite, bauxite, and alumina) were selected based on the most promising results from other researchers. The attapulgite clay used in past IRF trace metals studies was tested as the fifth sorbent. The sixth material, quartz, was selected as a "neutral" material, or system blank.

The approximate mineral content of diatomaceous earth, kaolinite, and bauxite are given in Table 1. Alumina is presumed to be pure Al_2O_3 and the attapulgite clay is a hydrated magnesium aluminum silicate $[(Mg,Al)_5Si_8O_{22}(OH)_4 \cdot 4H_2O]$ containing some dolomite $[Ca,Mg(CO_3)_2]$, calcite $[CaCO_3]$, and silica $[SiO_2]$. Quartz is presumed to be pure silica.

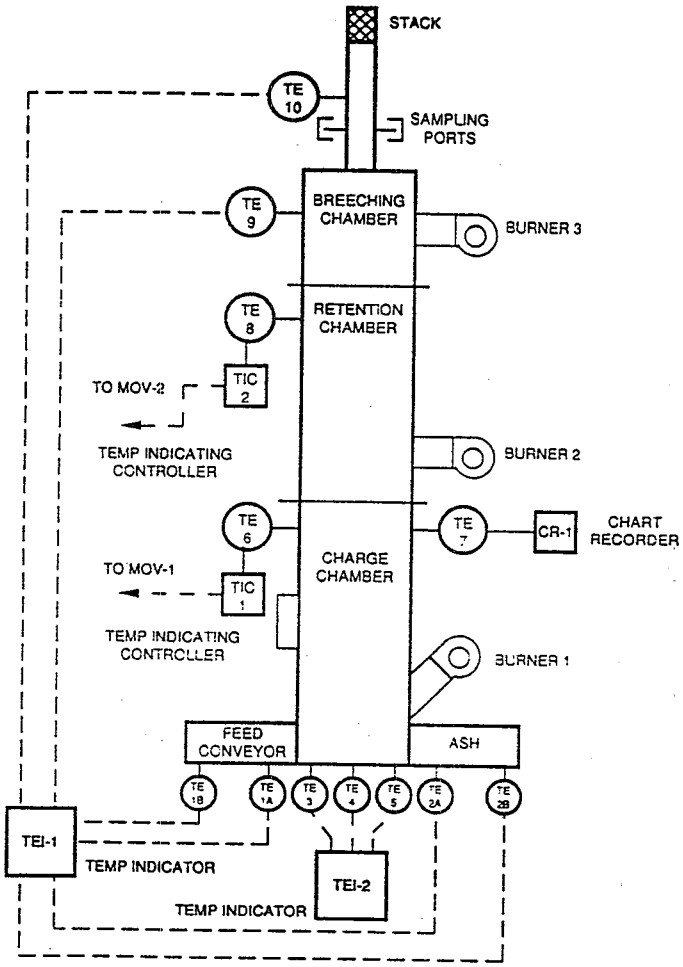

FIGURE 1. IRF THERMAL TREATABILITY UNIT (TTU)

TABLE 1. APPROXIMATE SORBENT MINERAL COMPOSITION

	Diatomaceous earth	Kaolinite	Bauxite
SiO_2	90.4	52	11
Al_2O_3	6.5	45	84
Fe_2O_3	2.3	1	5
TiO_2		2	
CaO	0.2		
MgO	0.3		
Other oxides	0.3		

Three solid bed temperatures were tested: 540°C, 700°C, and 870°C (1000°F, 1300°F, and 1600°F). Two feed chlorine contents were tested: 0% and 4% by weight. Polyvinyl chloride powder was added to the mixtures as the chlorine source.

Sorbent impact on the retention of the following trace metals was evaluated in the program: arsenic, cadmium, chromium, lead, and nickel. Two forms of incorporating the metals into the feed mixtures were evaluated. Past trace metals tests at the IRF have used aqueous metal spike solutions containing soluble nitrate salts of the metals (with the exception of arsenic which has been added as As_2O_3). For continuity, this form was one of the two used in the tests. The second form of metal spiking was a metal compound "dispersion". The dispersion consisted of metal compound powders suspended in a liquid carrier analogous to pigments dispersed in paint or ink. Chromium, cadmium and lead were present as metal oxides in the dispersion, while arsenic and nickel were introduced as sulfides and carbonates, respectively.

For each test, weighed amounts of the appropriate mixtures of sorbent, PVC (for tests with chlorine-containing feed), and metal spiking formulations were added to a TTU quartz tray. Charge depth was held constant at nominally 2 cm, corresponding to a charge volume in the tray of approximately 300 cm^3. Feed metal concentrations were also held constant as follows: arsenic (250 mg/kg); cadmium (50 mg/kg); chromium (150 mg/kg); lead (250 mg/kg); and nickel (150 mg/kg). Charge mass ranged from 50 g to 320 g, depending on sorbent bulk density.

Tray residence time in the TTU was approximately 20 minutes at the target solid bed temperature. Based on the results of other research, no further reaction between the sorbent and metals was expected after the first 10 minutes at target temperature.

Sampling and Analysis

For each test, TTU gas temperatures and solid bed temperatures were measured.

Samples of unspiked sorbent, aqueous metal spiking solution, metal dispersion, TTU feed, and TTU discharge were collected for metal analyses. Additionally, one TTU feed sample from each of the sorbent/metal formulation combinations and TTU discharge samples from every test were subjected to TCLP extraction, and the resulting leachates analyzed for trace metals.(2) Quality assurance samples were prepared as well.

Aqueous liquid samples were digested using EPA Method 3010.(3) Solid samples and the metal dispersion samples were digested using a microwave-assisted HNO_3/HF procedure.(4) Analyses of each of the latter digestates for arsenic were by Method 7060 [GFAA].(3) All other digestates analyses were by Method 6010 [ICAP].(3)

RESULTS/CONCLUSIONS

Tests were conducted from November through December 1993. Analytical results were not available as of the writing of this abstract. As available, results and conclusions will be discussed during the Symposium presentation.

REFERENCES

1. Acurex Environmental Corp. Quality Assurance Project Plan for Evaluating the Effectiveness of Additives as Sorbents for Metal Capture Using the Thermal Treatability Unit. Contract No. 68-C9-0038, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1993.

2. Method 1311 Toxicity Characteristic Leaching Procedure (TCLP). 40 CFR Part 261, Appendix II.

3. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, 3rd Edition, Revision 1, U.S. Environmental Protection Agency, 1992.

4. Methodology for the Determination of Metals Emissions in Exhaust Gases from Hazardous Waste Incineration and Similar Combustion Processes. 40 CFR Part 266, Appendix IX.

FOR MORE INFORMATION

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ABSTRACT

"PILOT-SCALE INCINERATION TESTS OF UDMH AND NITROGEN TETROXIDE - FORMER SOVIET UNION LIQUID BALLISTIC MISSILE PROPELLANTS"

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This is a summary report of a particularly interesting and unusual missile propellant incineration research project conducted at the U.S. EPA's Incineration Research Facility (IRF) during the winter of 1993-94. Data generated from these recent pilot-scale incineration tests were useful toward the goal of international peace - toward the elimination of propellants from some of the world's strategic offensive arms. The presentation will begin on a brief historical note as follows.

On April 4, 1993, Presidents Clinton and Yeltsin agreed in principle to a draft agreement between the U.S. Department of Defense (DOD) and the Committee for Defense Industry of the Russian Federation concerning cooperation in the elimination of Russian Strategic Offensive Arms. This agreement was signed and became effective on August 26, 1993. The agreement obligates the DOD to provide the Russian Federation with an extensive list of equipment for the Federation's use in eliminating strategic offensive arms in accordance with schedules negotiated in the Strategic Arms Reduction Treaty (START). Included in this equipment list are mobile incinerators, each capable of destroying at least 750 metric tons per year of ballistic missile liquid propellant comprised of unsymmetrical dimethyl hydrazine (UDMH) fuel and nitrogen tetroxide (N_2O_4) oxidizer.

DNA supported a series of tests at the EPA's IRF to demonstrate that the exact U.S. chemical equivalents of Russian Ballistic missile propellant fuel and oxidizer can be incinerated effectively and safely and in compliance with applicable U.S. and Russian environmental laws and regulations. The tests successfully obtained certain technical information which is helping the U.S. to commercially procure the incinerators.

DNA selected the U.S. Environmental Protection Agency (EPA) Incineration Research Facility (IRF) at Jefferson, Arkansas to conduct the tests. The presentation will describe the specific test program objectives and the test conditions for the tests, etc. The sampling and analysis procedures used to satisfy the test objectives will also be described.

The test program was conducted in the rotary kiln incineration system (RKS) at the IRF which consists of a primary combustion chamber, a transition section, and a fired afterburner chamber. The primary combustion chamber, or kiln, is nominally 1.04 m (3 ft-4.75 in) in diameter and 2.26 m (7 ft-5 in) long. The afterburner is nominally 0.91 m (3 ft) in diameter and 3.05 m (10 ft) long. A 4.43-m (14 ft-6.5 in) long, 0.61-m (2-ft) diameter refractory-lined afterburner extension follows the afterburner and allows isokinetic sampling of hot flue gas prior to quenching. Both the kiln and afterburner are fitted with 590 kW (2 MMBtu/hr) auxiliary fuel burners. Natural gas was the auxiliary fuel, although liquid waste or fuel can also be fired as was the case for these tests. Typical firing rates are 290 to 440 kW (1.0 to 1.5 MMBtu/hr) to the kiln and 440 to 590 kW (1.5 to 2.0 MMBtu/hr) to the afterburner.

After exiting the afterburner, flue gas flows through a quench section followed by a primary air pollution control system (APCS). The primary APCS for the planned tests was a venturi scrubber/packed-column scrubber combination. This scrubber system removed most of the particulate and acid gas, such as HCl, SO_2, or NO_2, in the flue gas. Downstream of the primary APCS, a backup secondary APCS, comprised of an activated-carbon adsorber and a high-efficiency particulate air (HEPA) filter was in place. This secondary APCS ensured that RKS stack emissions were acceptable even under incineration failure conditions.

The objective of the Phase I tests were to establish that UDMH and N_2O_4 can be destroyed in an incineration system in a manner that meets U.S. and Russian environmental regulations. The applicable U.S. environmental regulations are the hazardous waste incinerator performance standards established under the Resource Conservation and Recovery Act (RCRA). These standards require that the incinerator achieve:

- At least 99.99 percent destruction and removal efficiency (DRE) of the principal organic hazardous constituents (POHCs) in the waste feed to the incinerator
- HCl emissions of no more than 1.8 kg/hr or 1 percent of the HCl entering the incinerator's APCS, whichever is greater

The promulgated regulations require that particulate emissions be no greater than 180 mg/dscm (0.08 gr/dscf) corrected to 7 percent O_2. However, recent EPA guidance, planned for incorporation into hazardous waste

incinerator operating permits as they are issued or renewed, states that particulate emissions be limited to 34 mg/dscm (0.015 gr/dscf) corrected to 7 percent O_2.

In addition, hazardous waste incinerator permits currently being enforced in the U.S. require that CO emissions be no greater than a 1-hour rolling average of 100 ppm, corrected to 7 percent O_2, and limit hazardous constituent trace metal feedrates to levels designed to prevent exceeding risk-based ambient levels. The hazardous constituent trace metals are antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, and thallium. Finally, current guidance states that emissions of total tetra- through octa-chlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs) be limited to 30 ng/dscm corrected to 7 percent O_2.

Discarded or off-specification UDMH to be destroyed or disposed of would be the listed hazardous waste U098. The POHC for this waste for which an incinerator would need to achieve 99.99 percent DRE or better is the UDMH itself. Discarded or off-specification N_2O_4 would be listed waste P078. P078 is listed as nitrogen dioxide (NO_2). Although N_2O_4/NO_2 is not an organic constituent, requiring 99.99 percent N_2O_4/NO_2 DRE or better was thought to be an appropriate incinerator requirement.

The Russian environmental regulations limit the emissions of UDMH as well as several potential UDMH products of incomplete combustion (PICs) from the incineration of UDMH. The limits are occupational exposure limits in terms of maximum permissible concentrations in workplace air.

The test program consisted of a series of individual incineration tests. Three tests were performed under the same incineration system operating conditions feeding each component of the missile propellant. Triplicate testing is a requirement for U.S. hazardous waste incinerator trial burns. In addition, triplicate testing establishes a measure of confidence in test results by allowing the precision of the test program sampling and analysis procedures to be evaluated. Two sets of triplicate tests feeding UDMH (six total) were required to complete all the flue gas sampling procedures for the UDMH feed tests. Thus, nine tests in total, six feeding UDMH and three feeding N_2O_4, were performed.

The tests showed that environmentally acceptable incineration could be achieved under at least one set of incineration conditions, although perhaps not the optimum set of conditions.

The UDMH destruction tests were performed at kiln exit gas temperature of 980°C (1,800°F). Only UDMH was fed to the kiln along with the required atomization media and combustion air. The RKS auxiliary fuel, natural gas, was zero during actual testing, although natural gas was used for incinerator heat up, and to maintain incinerator temperatures overnight between tests. UDMH was fed to the kiln via the liquid waste/fuel nozzle of the kiln's dual fuel burner. The UDMH was directly pumped and metered from its nitrogen-blanketed storage container to the burner nozzle.

The N_2O_4 destruction tests were also performed at a kiln exit gas temperature of 980°C (1,800°F). Diesel fuel served as the material to be

oxidized by N_2O_4 for its destruction. The diesel fuel was fed to the kiln via the liquid nozzle of the kiln's dual fuel burner. The N_2O_4 oxidant was added to the burner primary air supply.

The mode of operation will require an N_2O_4 evaporator between the N_2O_4 storage container and the kiln burner, which delivered N_2O_4 vapor to the burner air supply line. The evaporator was fed from the N_2O_4 storage container by pressurization of the storage container nitrogen blanket. Evaporator discharge vapor temperature was maintained at 32°C (90°F), comfortably above the N_2O_4 boiling point of 21°C (70°F). The N_2O_4 supply line to the kiln burner air supply line was heat-traced to ensure that no N_2O_4 recondensation occurred. The feed line was connected into the burner primary air supply line at the kiln burner.

For all test feeds, the RKS afterburner was fired with natural gas to maintain an afterburner exit gas temperature of 1,090°C (2,000°F). The IRF hazardous waste management permit specifies a minimum afterburner temperature of 1,017°C (1,863°F) whenever a hazardous waste is being fed to the system. The 1,090°C (2,000°F) set temperature was chosen as a typical afterburner operating temperature, and that level also allowed a margin of flexibility above the permit-mandated temperature.

Heat balance calculations were performed to estimate firing rates associated with the target incinerator operating conditions. The heat of combustion of UDMH is 33.0 MJ/kg (14,200 Btu/lb); that of typical diesel fuel is 45.3 MJ/kg (19,500 Btu/lb). The heat of reaction of diesel fuel and N_2O_4 is about 45.7 MJ/kg of diesel fuel (19,700 Btu/lb).

For all tests, the RKS scrubber system was operated at its nominal design conditions and at as close to total recirculation (zero to minimum blowdown) as possible. Flow rates required to achieve the target kiln and system operating conditions were based on scoping tests. These scoping tests explored the ability to safely achieve stable incinerator operation and will be discussed in greater detail in the presentation.

EVALUATION OF A ROTARY KILN INCINERATOR AS A THERMAL DESORBER

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INTRODUCTION

Incineration is a common means of treating soils at Superfund sites contaminated with organic hazardous constituents. Low to moderate thermal desorption is alternative technology. Operation of a rotary kiln incinerator in the temperature range of a thermal desorber is an attractive application for the remediation of soils. EPA decided to investigate such a possibility at its Jefferson, AR, rotary kiln incinerator site. Advantages of operation in the low to moderate temperature range include less fuel consumption, avoidance of slag formation, and less likelihood of volatilizing trace metals that may be in the soil.

The objectives of the test program designed by EPA and its contractor were to study the effects of five parameters believed to be of primary importance in decontaminating soils containing organics and trace metals. Test parameters included: soil moisture content, treatment temperature range, treatment time, solids bed depth, and degree of solids agitation. This paper is limited to reporting preliminary results on: moisture content, treatment temperature versus type compound (i.e., volatile vs. semivolatile), and soil feed rate versus treatment time.

METHODOLOGY

A synthetic feed material was prepared using a mixture of local top soil and clay. The organic contamination was achieved by mixing nine organics ranging from volatile (benzene) to semivolatile (pyrene) compounds (see Table 1) and adding this mixture to the soil. Soil moisture contents of 10 and 20 percent were selected for testing. Soil moisture content was held constant while the other test parameters were varied by changing the operating conditions of the incinerator. These conditions were changed from test to test by varying the contaminated soil feed rate, kiln exit gas temperature, and kiln rotation rate. Twelve tests under 11 different combinations of test variables were performed; one duplicate test was performed.

Test combination targets consisted of: three different kiln exit gas temperatures (320°C, 480°C, and 650°C), two soil feed rates (70 and 210 kg/hr), and three kiln rotation speeds (0.2, 0.5, and 1.5 rpm). The peak solids bed temperature was achieved by changing the kiln exit gas temperature. Bed temperatures corresponding to the above exit gas temperatures were about 120°C, 270°C, and 430°C (see Table 2). Residence time was achieved by varying the kiln rotation speed. Total kiln solids residence times corresponding to the above kiln rotation speeds were 60, 40, and 30 minutes, respectively. Solids bed depth was affected by both feed rate and kiln rotation speed.

To allow for a more thorough evaluation of treatment effectiveness at varying treatment times for each test condition, samples of the solids bed material were taken at four axial locations along the kiln, in addition to a solids discharge sample. These samples corresponded to four

different treatment times for each test condition.

RESULTS/CONCLUSIONS

A summary of achieved operating parameters and resulting test conditions is given in Table 3. As noted by comparing Tables 2 and 3, target test conditions were met in most cases, especially for the exit gas temperatures. As noted in the Introduction, the results reported in this paper are limited to the effectiveness of treatment by comparing bed temperature vs. kiln exit temperature; treatment temperature vs. type of compound; soil feed rate vs. type of compound; and the effect of moisture on degree of treatment.

The effect of moisture at the different kiln operating temperatures with the low feed rate is depicted in Figures 1a through 1f. By examining Figure 1, one can see that moisture affected the treatment of benzene very little at any of the kiln temperatures, while for pyrene the higher moisture content shifted the time required for desorption of pyrene significantly to the right. Moreover, a minimum of about 20 to 30 minutes is needed for the bed temperature to vaporize the moisture before treatment of the volatile organic compounds can be effected.

At lower operating temperatures high moisture content has a noticeable effect on the volatile compound, benzene, while little noticeable difference is indicated for the semivolatile compound, pyrene. Thus, depending on operating temperatures, moisture definitely adversely affects the reduction of organic compounds from soils. For the semivolatile compounds, only about 99.5 per cent reduction is achieved regardless of the kiln temperature.

Figure 2a-d is a depiction of the effect of feed rate on the effectiveness of treatment. Obviously, the faster feed rate adversely affects the reduction of pyrene. This results from the insufficient time for the bed temperature to reach a level necessary for the semivolatiles to be volatilized. Even benzene is affected at the lower temperatures.

The results to date indicate effects that were expected. More analysis will be performed prior to the presentation of the paper and the additional analysis will be available at the Symposium.

TABLE 1. ORGANIC CONSTITUENTS IN THE SYNTHETIC CONTAMINATED SOIL

Compound	Molecular weight	Specific gravity	Melting point, °C	Boiling point, °C	Organic liquid mixture composition, wt %	Concentration in soil at an organic liquid fraction of 2%, mg/kg
n-Hexane	86.2	0.66	-94	69	15	3,000
Benzene	78.1	0.88	6	80	15	3,000
Toluene	92.7	0.87	-95	111	15	3,000
Tetrachloroethene	165.9	1.62	-22	121	24	4,800
n-Octane	114.2	0.70	-57	126	15	3,000
Chlorobenzene	112.6	1.11	50	132	10	2,000
Naphthalene	128.2	1.16	80	218	3	600
Phenanthrene	178.2	1.18	100	340	2	400
Pyrene	202.2	1.27	156	404	1	200

TABLE 2. TARGET TEST CONDITIONS

Test	Kiln exit gas temperature, °C (°F)	Expected peak solids bed temperature, °C (°F)	Kiln rotation rate, rpm	Soil feedrate, kg/hr (lb/hr)	Soil moisture content, %
1	320 (600)	120 (250)	0.2	70 (150)	10
2	480 (900)	270 (520)	0.2	70 (150)	10
3	650 (1,200)	430 (800)	0.2	70 (150)	10
4	320 (600)	120 (250)	0.2	70 (150)	20
5	480 (900)	270 (520)	0.2	70 (150)	20
6	650 (1,200)	430 (800)	0.2	70 (150)	20
7	480 (900)	270 (520)	0.5	70 (150)	10
8	480 (900)	270 (520)	0.5	70 (150)	20
9	480 (900)	270 (520)	1.5	70 (150)	20
10	480 (900)	270 (520)	0.2	210 (470)	10
11	480 (900)	270 (520)	0.2	210 (470)	20
12	480 (900)	270 (520)	0.2	70 (150)	10

TABLE 3 ACTUAL TEST OPERATING CONDITIONS

Test Date	1 1/29/93	2 2/2/93	3 2/4/93	4 1/27/93	5 12/4/92	6 12/16/92	7 1/6/93	8 12/9/92	9 2/11/93	10 1/15/93	11 1/19/93	12 1/21/93
Average soil feedrate,												
kg/hr	68	70	67	69	73	71	67	78	66	215	214	67
(lb/hr)	(149)	(155)	(147)	(153)	(160)	(157)	(148)	(171)	(145)	(473)	(471)	(148)
Kiln exit gas temperature												
Range, °C	305-331	474-492	641-658	301-330	463-499	633-660	471-494	467-501	471-492	287-508	464-500	471-493
(°F)	(501-627)	(885-918)	(1,185-1,216)	(524-626)	(866-930)	(1,171-1,220)	(880-921)	(873-935)	(880-918)	(548-946)	(867-932)	(879-919)
Average, °C	317	482	648	316	482	648	482	480	482	481	482	482
(°F)	(603)	(900)	(1,199)	(601)	(900)	(1,199)	(900)	(896)	(900)	(897)	(900)	(900)
Kiln rotation rate, rpm	0.2	0.2	0.2	0.2	0.2	0.2	0.5	0.5	1.5	0.2	0.2	0.2
Total kiln solids residence time, min	58	67	70	64	61	54	60	29	27	36	42	63
Average solids bed temperature at "x" m ("x" ft) from feed face, °C (°F)												
0.6 (2.0)	86 (186)	123 (253)	267 (512)	69 (156)	113 (235)	122 (251)	144 (292)	179 (355)	172 (341)	130 (266)	107 (224)	144 (291)
1.1 (3.5)	109 (228)	182 (359)	393 (740)	88 (191)	204 (399)	319 (606)	204 (400)	215 (419)	194 (382)	161 (321)	132 (269)	211 (412)
1.5 (5.0)	115 (239)	228 (443)	434 (814)	98 (208)	260 (500)	401 (753)	249 (481)	239 (462)	245 (473)	175 (347)	149 (300)	257 (495)
2.0 (6.5)	123 (254)	227 (440)	451 (844)	123 (254)	182 (359)	356 (672)	241 (465)	231 (448)	277 (531)	253 (487)	239 (463)	244 (471)

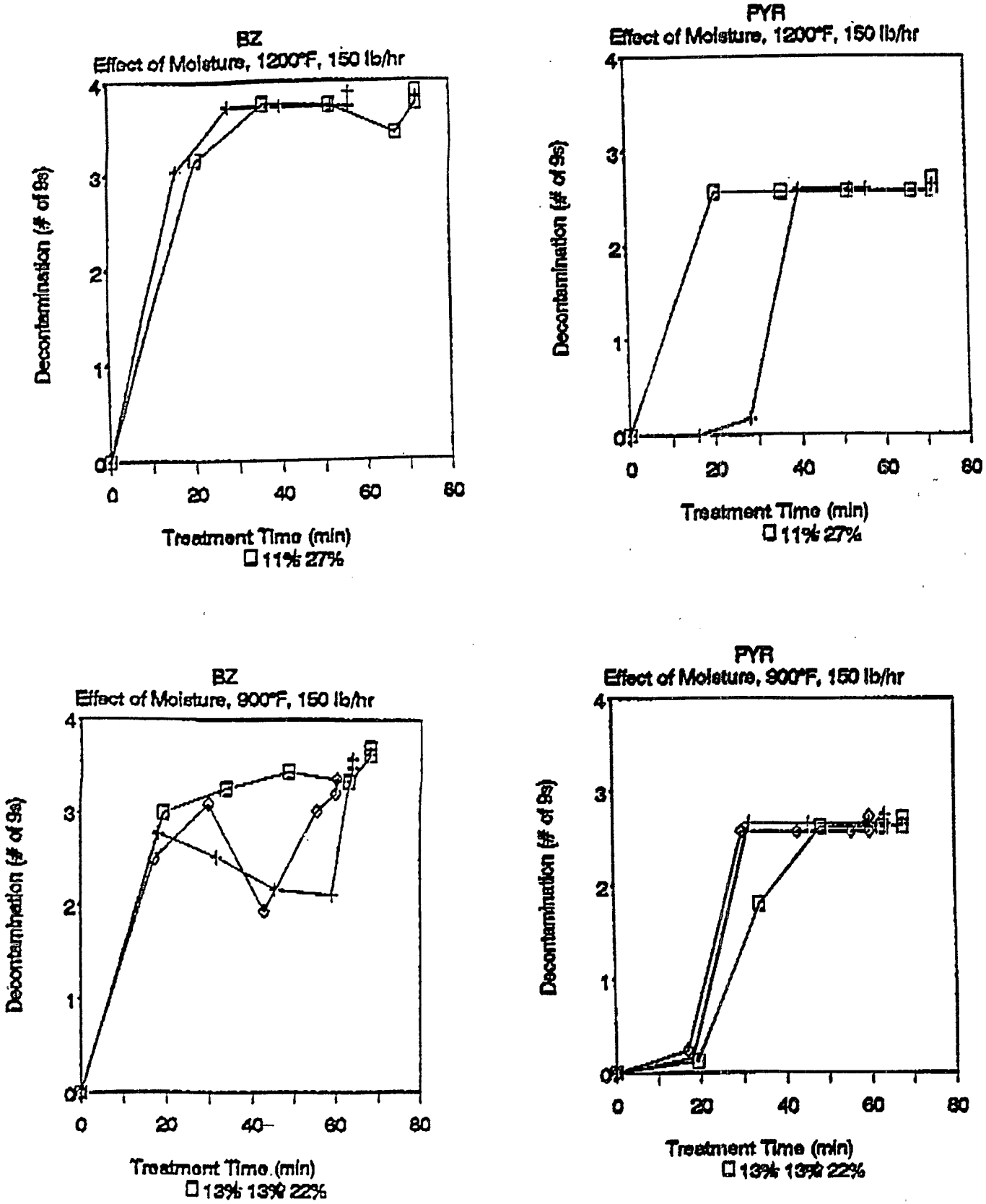

Figure 1a-d. Effect of Moisture vs. Kiln Exit Temperature (Low Feed Rate)

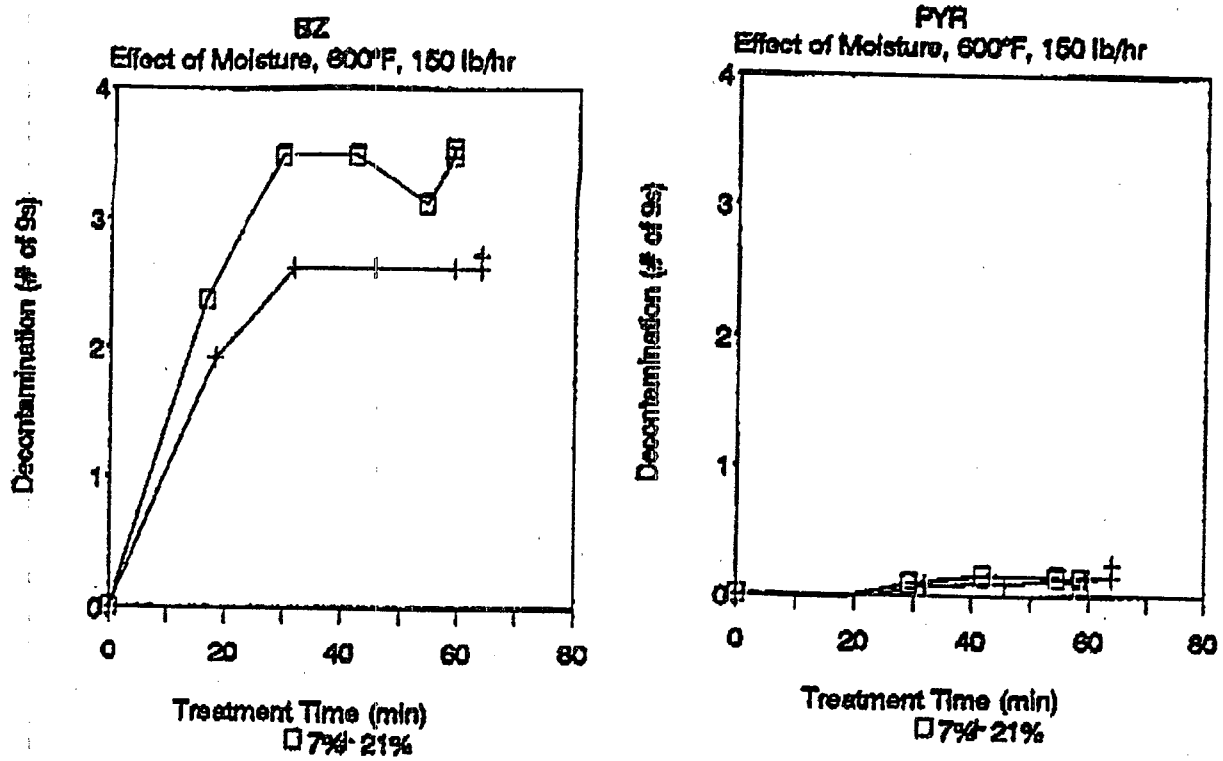

Figure 1e-f. Effect of Moisture vs. Kiln Exit Temperature (Low Feed Rate)

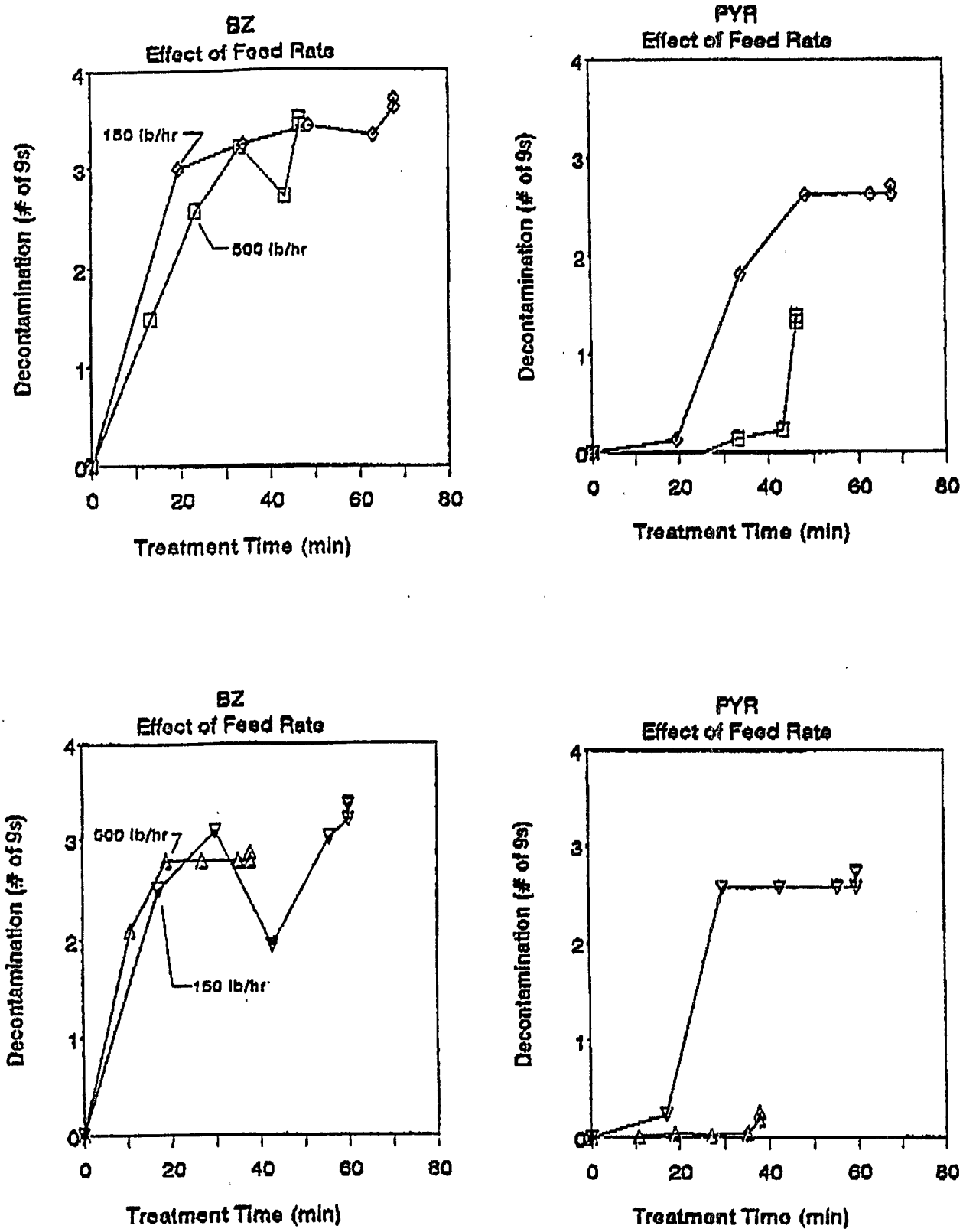

Figure 2a-d. Effect of Waste Feed Rate on Organic Treatment

RESULTS OF THE MITE PROGRAM'S MATERIAL RECOVERY FACILITY (MRF) EVALUATIONS

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INTRODUCTION

Increasing environmental concern over the disposal of municipal solid waste (MSW) in the United States has prompted municipalities to increase recycling activities in order to conserve natural resources and minimize the amount of solid waste requiring disposal. Material Recovery Facilities or "MRFs" have become a major component in solid waste recycling systems. A MRF is a facility that accepts commingled recyclables (such as plastic, glass, paper and aluminum) and processes the material for market. The incoming materials are collected at the curbside, usually from a bin or bag, and delivered directly to the MRF for processing. There are over 200 MRF's in the United States, and facilities are continually being sited and built.[1] MRF designs vary greatly depending on the requirements of the individual recycling program, economic constraints of the municipality, and the solid waste generation rate of the area.

This evaluation is being conducted under the auspices of the Municipal Solid Waste Innovative Technology Evaluation (MITE) Program. The purpose of the MITE program is to provide objective, third party evaluations of solid waste management and recycling technologies and transfer this information to municipalities and the public sector. The purpose of the MRF evaluation is to gather data and information that will answer the many questions that still exist regarding MRFs. Though MRFs are continually being sited and built, there has been no in-depth evaluation of existing facilities, examining potential environmental problems and quantifying their impact on the existing solid waste management system.

For the purposes of this evaluation, it was decided that a cross-section of facilities was necessary to address the full range of operating characteristics. The MITE evaluation includes six facilities, differing in size, ownership (public or private), geographic area, and separation scheme. The six facilities that volunteered to participate in this study include:

- Islip, New York
- Montgomery County, Maryland
- Albuquerque, New Mexico
- Hartford, Connecticut
- Rice County, Minnesota
- Orange County, Florida

In order to adequately address the pertinent environmental and economic issues, each evaluation consists of the following four components:

- Sampling of the air quality within and surrounding the facility.

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[1] Materials Recovery and Recycling Yearbook: Directory & Guide 1992-1993

- A material mass balance and calculation of recycling rate.
- Calculation of the energy requirements, including the collection, separation, and transportation of the recyclable material.
- Documentation of the capital and operational costs, within the full integrated solid waste management system.

The results of this study will be used to provide municipalities and others with information on successful programs, and to assist in economical and environmentally safe facility design and operation.

METHODOLOGY

A program plan was prepared considering the four components of the study. Each MRF evaluation consisted of two distinct parts: 1) a five day on-site evaluation that included interviews with facility managers and environmental sampling, and 2) a questionnaire, which gathered the other needed information on capital and operating costs, energy consumption, and recycling and recovery rates. The same evaluation plan was used for each MRF selected.

On-Site Evaluation

The facilities were approached and selected by the Solid Waste Association of North America (SWANA), and a planning visit was conducted by the sampling team prior to any project scheduling. Each facility operated under a specific sampling plan, tailored to the design and operating practices of that specific facility. The sampling plans underwent quality assurance review as well as review by the facility operators. The MRF operator review information was made available to help ensure that all parties were informed about what measurements would be taken.

The facility sampling consisted of three types of environmental measurements: ambient outdoor sampling, ambient indoor sampling, and personnel sampling. The ambient outdoor measurements were taken at the facility fenceline to ensure the inclusion of emissions from truck traffic with three outdoor sampling stations established, one upwind of the facility and two downwind. Inside the MRF both grab samples and personnel samples were taken. The personnel sampling was performed using monitors worn by selected personnel who were chosen as to represent different job tasks inside of the MRF. In addition to the measurement of particulate and gaseous contaminants, noise measurements were taken, both outside and insides the facility.

Since there was a lack of literature data on any of these contaminants in relation to MRFs, it was decided that a large list of measurements would be used for the first two facilities. Based on the results shown from the first two facilities, the list would be reduced by eliminating the measurements in which non-detectable levels of contaminants were found. The services of an Industrial Hygienist were used to determine which measurements were most appropriate. The reduced sampling plan was established and used at the remaining four facilities. The field sampling team retained the flexibility of adding any of the eliminated measurements, if there was the potential for detectable levels of that particular compound to be present. Table 1 outlines the full list of contaminants, where the measurements were taken and what measurements were retained in the Phase II testing.

EPA sampling and analytical methods were used as appropriate and all indoor contaminants were measured using the appropriate National Institute of Occupational Safety and Health (NIOSH) test methods.

TABLE 1. ENVIRONMENTAL MEASUREMENTS

Contaminant	Measurement Location		Status for Phase II
	Exterior	Interior	
Total Suspended Particulates	X		X
PM10	X		X
Lead (Pb)	X	X	X
Carbon Monoxide (CO)	X	X	X
Mercury Vapor (Hg)	X	X	X
Acetone	X		VOCs reduced to one day only
Benzene	X		
MEK	X		
Methyl Chloride	X		
Toluene	X		
TCA	X		
Xylenes	X		
Noise	X	X	X
Total/Respirable Dust		X	X
Pesticides		X	Reduced level of sampling
Metals (Al, As,Cr, Ni)		X	Eliminated due to non detectable levels
Crystalline Silica		X	X
Microbiological	X	X	X

Economic Assessment

A two part questionnaire was developed by project personnel and the contractor, Roy F. Weston, Inc. and sent to each facility operator. The purpose of Part 1 of the questionnaire was to document the cost elements of the integrated solid waste management system, including capital and operating expenses, as well as education and outreach. The purpose of Part 2 was to gather data on energy requirements, by collecting information on the electricity required for facility operation and fuel consumption for transportation. This energy consumption/generation information is to be collected for all components of the solid waste management system, including disposal components such as landfills or waste-to-energy systems. The questionnaires are being compiled and interviews with solid waste department will be conducted to fill in any data gaps that exist.

RESULTS AND CONCLUSIONS

The evaluation was set up to complete sampling at two facilities using the full range of tests and measurements outlined previously. After receiving the results of these tests, areas in which no detectable levels were found were eliminated from further testing. This allowed project costs to be reduced without jeopardizing the integrity of the sampling plan. It should be noted that elevated levels of crystalline silica and aluminum have not been found, and these measurements were retained in the sampling plan, since glass and aluminum containers are present in every feedstock.

A conclusion that has already been reached, prior to final data analysis, is that no two facilities are the same, even if the design characteristics are identical. Each system must be designed and adapted within the framework of the integrated solid waste management system that already exists. Flexibility has also arisen as a major issue. The more successful MRFs are those that are designed to be flexible in response to changing recycling markets and market conditions. This allows for changes in processing requirements and making the facility more able to meet changes in markets.

One of the more difficult tasks of this project is documenting the costs associated with the individual systems. Each facility has different approaches to accounting, financing, facility ownership and operation. Different contractual arrangements are negotiated based on the needs of the individual municipality or solid waste management district. Placing these costs on a level playing field in order to document the true cost of recyclable collection and processing has proven to be a difficult task.

A report will be published based on the results of this evaluation. The report will outline the major findings and conclusions of the project. The purpose of the report is to assist solid waste officials in their decision making process, and expose them to technologies and approaches that they are currently unfamiliar with. This evaluation can be used as a tool to educate the solid waste decision official on the ranges of technology that are available.

REFERENCES

1. Berenyi, E. Gould, R. Materials Recovery And Recycling Yearbook: Directory & Guide 1992-1993. Government Advisory Associates. 1992.

2. Peer Consultants, P.C. Material Recovery Facilities for Municipal Solid Waste. EPA/625/6-91/031, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1991.

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FULL-SCALE LEACHATE-RECIRCULATING MSW LANDFILL BIOREACTOR ASSESSMENTS

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INTRODUCTION

The integrated waste management hierarchy philosophy continues to develop as a useful tool to solve solid waste issues in an environmentally responsible manner. Recent statistics indicate that approximately two thirds of municipal solid waste in the United States is disposed in landfills. EPA research has continued to develop and refine the variety of technologies, materials, and operational techniques to further reduce risk from this most often used form of waste disposal.

Current landfill operational technique involves the preparation of a waste containment facility, the filling of the waste unit, installation of the final cover, and the maintenance of the unit. The goals being to isolate the waste from people, and to minimize infiltration of water, thus minimizing releases of moisture and decompositional gases into the environment. This method of operation has proven to be reasonably effective in waste disposal, effectively minimizing risk by collecting the liquid that percolates through the waste, called leachates, at the bottom of the landfill, and controlling landfill gas with collection systems. Effective gas collection often results in utilization of the gas for other purposes.

Concerns over the longevity of containment systems components present questions that cannot be answered without substantial performance data. Landfills, as currently operated, serve to entomb dry waste. Therefore, the facility must be maintained in perpetuity, consuming funds and ultimately driving up waste collection costs. Further, there is a concern about rare but possible environmental impacts from leakage through lining or cover components and possible catastrophic failures of the landfill system.

This presentation will describe a new form of solid waste landfill operation, it is a technique that involves controlled natural processes to break down landfilled waste, and further minimize risk to human health and the environment.

A landfill operated in an active manner will encourage and control natural decomposition of landfilled waste. This can be accomplished by collecting leachate, and reinjecting it into the landfilled waste mass. Keeping the waste mass moist will lead to a largely anaerobic system with the capacity to rapidly stabilize the landfilled waste mass via physical, chemical and biological methods. The system has proven the ability to breakdown portions of the waste mass, and to degrade toxic materials at the laboratory scale.

METHODOLOGY

Experiments are designed to compare similar landfill cells as each is operated in a different manner, either wet or dry. The experiments are time consuming and require long-term commitment to research. The projects are also very costly because of their magnitude. To gather data and analyze results, U.S. EPA embarked on a research program to study this operational technique for MSW landfills in the early 1980s. Bench-scale laboratory research on the anaerobic bioreactor in MSW landfills was conducted with the assistance of The Georgia Institute of Technology (1). Researchers found that by simply reinjecting common MSW landfill leachate under controlled sequences that the

following benefits could potentially be realized at full scale:

- expansion of landfill capacity through volume reductions induced by biological decomposition of MSW in the landfill, reducing the actual number of landfills that must be sited

- improved quality and quantity of recoverable landfill gases (methane and carbon dioxide) through controlled biological reactions

- toxicity reduction of the MSW mass through biological decomposition and immobilization in the waste mass resulting in lower pollutant concentration in leachate

- reduced post-closure monitoring time due to toxicity reduction

Building upon this fundamental research, EPA sponsored further research to take this operational technique to the field in the form of pilot-scale landfill test cells (2). Anticipating the opportunity to build on this research, full-scale landfills were sought and selected to prove the technology at full-scale. One landfill was selected near Gainesville, Florida, and another landfill project is in the construction phase near Rochester, New York.

Table 1. U.S. EPA Landfill Bioreactor Projects in 1994

Location	Scale	Description	Status	Ref
Georgia	Lab	Model Landfill Lysimeters	Completed '93	1
Delaware	Pilot	Test Cells 2 each, 1 acre each, wet vs. dry	Covered	2
Florida	Full	Active Fill - 6 acres	Filling	3
New York	Full	Active Fill - 10 acres	Filling	4
Ohio	Full	Remediation of Existing Landfill	Planning	5

In addition to these activities, EPA is tracking related projects in the United States, and around the world. EPA is also pursuing the application of this technology in a remedial manner at an unlined, uncontrolled landfill.

Leachate-Recirculation Process

Prototype methods which have been utilized to date include surface spraying, surface ponds, vertical injection wells with and without wicks, and horizontal surface infiltration devices. Generally, additional costs for leachate recirculation materials are relatively low. For proper execution of a leachate recirculation system at a modern MSW landfill, the following components are generally considered to be necessary:

- a composite lining system comprised of a single or double composite compacted soil and a geomembrane, with leachate handling system.

- MSW placed at a density determined to accommodate leachate recirculation

- daily cover that does not significantly affect the continuous passage of moisture through the landfill from top to bottom (this rules out many traditional MSW landfill daily cover practices)

- a leachate reintroduction system that is concealed within the landfill enclosure, that only uses native landfill leachate
- an active gas collection system as part of a comprehensive landfill cap design
- a landfill cover capable of providing modern landfill cap functionality, that can maintain integrity as the leachate recirculation process causes landfill volumes to decrease,
- a trained landfill operator who understands the daily operational requirements of a leachate-recirculating landfill

Many of these issues remain as engineering challenges that need to be resolved in full-scale implementation.

The leachate-recirculation process is fundamentally simple, requiring relatively minor changes over the current designs. However, the number of variables involved to demonstrate control over the reactions in these studies are numerous, and every attempt is made during experimental design to control the number of variables. Operator training is critical, and outputs from these projects are aimed at operator control. As a matter of practicality, experiments to evaluate materials that may be added to the landfill during filling to enhance degradation have been relegated to future experimentation. Possible additions include waste pre-processing, microbiological additives, waste sludge, gases, or the control of temperature of the waste mass.

Concurrent with EPA research, other research projects are underway in the USA and around the world. There are new projects being initiated in California, Florida and New Hampshire, and underway around the world in Canada, Germany, Denmark, Italy, Sweden, Japan, and United Kingdom. The collective database formed in the study of these landfills will supply enough information to assess the performance of this operational technique in the field.

Landfilling in the Future

As landfills continue to evolve as sophisticated waste disposal and decomposition facilities, there are new goals anticipated for the future. Foreseen is a waste management park that will involve centrally located management of a variety of waste streams, of which a landfill will provide a necessary service. Waste water, sludges, composted waste and green waste, MSW materials recovery facilities, incinerators, and recycling facilities require inputs and outputs that can be integrated resulting in more efficient processing of MSW.

The landfill could produce an output of low to medium grade compost that could be used for soil amendments in roadways and earth works. Gas from the landfill could be used to generate electricity or power collection vehicles. The landfills could be arranged in a turntable-type arrangement so that cell #1 of the landfill can be constructed, filled, covered, and placed under leachate recirculation, then on to cell #2, where the process is repeated, and so on. When all cells are complete, the operator returns to cell #1, where the contents could be mined (7), with recyclables and compost removed, the bottom lining inspected and replaced when necessary, and the entire process again. While this technique will likely not eliminate the need to site new landfills, it will significantly increase the useful life of landfills when constructed to operate as bioreactors.

RESULTS

The status of active EPA sponsored projects are described here. The effort has benefitted from the active participation of major waste management companies in the USA, and from the

collaborative research efforts of EPA's colleagues, and their participation is gratefully acknowledged. Results to date are derived from the following projects:

Laboratory Lysimeter Studies

Completed in 1993, the research performed at the Georgia Institute of Technology and University of Pittsburgh showed leachate recirculation offers rapid and complete stabilization of the landfilled waste masses. The system proved resiliency to toxic loadings that caused retardation but not defeat of the stabilization process. The study showed that landfills are capable of biological and physicochemical reactions to attenuate waste constituents via reduction, precipitation, and matrix capture for heavy metals, and biotic and abiotic transformation, and sorption for organic materials. The study also showed that the performance of the bioreactor landfill can be monitored with leachate and gas parameters during significant phases of the reaction. The study concluded that the bioreactor landfill design is viable, and offers a significant improvement over traditional landfill operation (1).

Pilot-Scale Landfill Test Cells - Delaware

Two 1-acre pilot-scale landfill test cells are currently operated by the Delaware Solid Waste Authority in Sandtown, Delaware. Two identical cells were constructed, one operated traditionally (dry) and the other employing leachate-recirculation. The cells have been operating for approximately 1.5 years, and although the data is being analyzed, preliminary results have shown that the trends described in the early laboratory research are repeated in the field (2).

Full-Scale Landfill Project - Alachua County, Florida

The first of two full-scale landfill projects was selected near Gainesville, Florida. The landfill is operated by the City with assistance from The University of Florida, engineering firms, and others. The landfill is approximately half full, and leachate recirculation systems are being installed as filling progresses. A nearby landfill at that site has performed this technique in a less sophisticated manner, utilizing surface infiltration ponds in previous years with success (3).

Full-Scale Landfill Project - Monroe County, New York

The second full-scale landfill project is in the construction phase near Rochester, New York. EPA is assisting the New York State Energy Research and Development Authority (NYSERDA) in their efforts to study how this landfill operational technique may achieve complementary goals of environmental protection, and the potential for enhanced energy production through gas recovery (4).

Remediation Project - Ohio

An unlined landfill is under study in Cincinnati, Ohio for application of leachate recirculation as an alternative to pumping and treating groundwater at an uncontrolled pre-regulatory landfill. The project is significantly more complicated due to the absence of a bottom liner, but researchers are convinced that groundwater can be controlled and barriers can be constructed to accommodate leachate recirculation at the site (5). A feasibility study is in final draft status, and the project will soon enter its second phase to complete pre-construction details.

Comprehensive Study - University of Central Florida

A comprehensive evaluation of active landfill bioreactor projects is underway at the University of Central Florida (6). Researchers there are compiling data from these projects, other American projects, and data from projects from around the world by site visitation and interactions with specialty

groups like the International Energy Agency's Landfill Gas Expert Working Group. Specific projects aim to assess moisture distribution of the leachate into the waste mass through computer models. This will assist designers in the configuration of the injection system, and may lead to guidance on placed waste densities that will accommodate leachate recirculation. A conference is planned for the autumn of 1994.

CONCLUSIONS

Landfills are currently designed and operated to serve as containment systems. While originally designed to entomb waste, the modern landfill has evolved into a more technically advanced containment system, with sophisticated controls and operational techniques. The landfill of the future will be protective of human health and the environment, will degrade the waste mass in the landfill, and will be reusable, allowing the waste to be excavated for the cell to be inspected and refilled as part of an integrated waste management park.

REFERENCES

1. United States Environmental Protection Agency. 1993. *Behavior and Assimilation of Organic and Inorganic Priority Pollutants Codisposed with Municipal Refuse, Volumes 1 and 2.* EPA/600/R-93/137a and b (NTIS PB93-222198 and 93-222206). Risk Reduction Engineering Laboratory, Cincinnati, Ohio.

2. Vasuki, N.C. 1993. "Practical Experiences with Landfill Leachate Recirculation in Pilot and Field Scale Units, *Proceedings: 31st Annual International Solid Waste Exposition, Solid Waste Association of North America*, San Jose, California, August 3.

3. Townsend, T., and W. L. Miller. 1993. Alachua County Southwest Landfill Bioreactor Project, *Proceedings: Madison Waste Conference*, Madison, Wisconsin, September.

4. Babcock, J., and Reis, J. 1993. "Monroe County's Leachate Recirculation Project," Modern Double Lined Landfill Management Seminar, New York State Department of Environmental Conservation, Saratoga Springs, NY, March 2-4.

5. United States Environmental Protection Agency. 1993. *Leachate Recirculation for Remedial Action at MSW Landfills, DRAFT FINAL REPORT.* Risk Reduction Engineering Laboratory, Cincinnati, Ohio.

6. Reinhart, D. R., and Carson, D. A. 1993. "Full-Scale Application of Landfill Bioreactor Technology," *Proceedings: 31st Annual Solid Waste Exposition of the Solid Waste Association of North America*, San Jose, CA (August 2-5, 1993).

7. United States Environmental Protection Agency. 1993. *Evaluation of the Collier County, Florida Landfill Mining Demonstration.* EPA/600/R-93/163. Risk Reduction Engineering Laboratory, Cincinnati, Ohio.

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PROTOCOL - A COMPUTERIZED SOLID WASTE QUANTITY AND COMPOSITION ESTIMATION SYSTEM

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INTRODUCTION

Traditional sampling theory generally follows the following paradigm:

SAMPLE SELECTION - SAMPLE OBSERVATION - SAMPLE ESTIMATION.

Typically, the samples are chosen by an unbiased procedure, such as simple random sampling or systematic sampling where it is assumed that the population is already in random order. In the sample observation or data recording stage, it is further assumed that observation of the elements of the sample is an independent process, i.e., that there is no queue of sample elements building up, waiting to be observed while an observation on one sample element is being made. Unfortunately, these assumptions do not fit the circumstances when the problem is to estimate the quantity of solid waste arriving at a given site a specific point in an industrial or commercial process. For one thing, the sample comes to the investigator, which is the reverse of the situation commonly described in standard sampling textbooks. Since the investigator has no control over the arrival of the sample elements, the sample observation process often is far from independent.

METHODOLOGY

Consider a situation where it is desired to weigh a random or systematic sample of 10% of the vehicles arriving at a landfill. Suppose that it is feasible to weigh up to 10 vehicles per hour and that the average interarrival time of vehicles is 3.2 minutes. On the average then, with either random or systematic sampling, one vehicle would be weighed every 32 minutes. If it takes an average of 10 minutes to weigh a vehicle, then this is well within the capability of the sampling system. Unfortunately, vehicles do not have uniformly distributed arrival times. There may be peak arrival periods when the number of trucks arriving and to be sampled overwhelms the weighing capability and one is forced to "default" on weighing some of the vehicles selected by the sampling plan. One result is that fewer vehicles are weighed than the sampling plan calls for, thus reducing the precision of the estimate of solid waste quantity. More important, however, is that if the load weights of the defaulted samples differ appreciably from the nondefaulted samples, bias will be introduced. For example, at many landfills vehicles arriving toward the end of the day tend to have smaller load weights than those arriving at other times. Since fewer vehicles arrive towards the end of the day, the tendency would be to oversample these lightly loaded vehicles and to undersample the normally loaded vehicles arriving at peak hours, thus introducing a bias.

When the rate of arrival of vehicles is not uniform throughout the day, random samples will produce some intervals of little or no activity and others of frenzied activity. Once scales are rented and labor hired to make the observations, it makes little sense not to use the equipment and labor to the fullest extent possible. If one samples to the fullest extent of the sampling capability, not only can the bias can be removed mathematically by equations developed in this study, but the resulting estimate has a smaller variance than random or systematic sampling.

SEASONALITY

It is well-known that the quantity of solid waste generated varies significantly from month to month. Municipal solid waste generation, for example, is typically low during the months of January, February, November, and December, and peaks during June, July, and August, although there are some variations depending upon geographical location. Thus it is not sufficient to sample one week out of the year to estimate generation for the entire year. A Monte Carlo simulation was performed using actual data obtained from a Boston solid waste site. Two sampling protocols were simulated: (1) random sampling, and (2) systematic sampling. Sampling frequencies of from two to ten times per year were investigated. Systematic sampling was found to be superior to random sampling for all sampling frequencies except for a sampling frequency of two, where random sampling is identical to systematic sampling. At a sampling frequency of four times per year, for example, the coefficient of variation (i.e., the standard deviation as a fraction of the mean) of systematic sampling was only 56% that of random sampling.

SAMPLE WEIGHTS FOR COMPONENT ESTIMATION

Traditional sampling theory assumes that there are sampling elements, i.e., discrete entities comprising the population about which inferences are to be drawn. When it comes to sampling solid waste for composition, however, there are no such discrete entities. There is, for example, no such thing as a basic unit of paper or of textiles. Thus, sampling procedures based upon discrete distributions (such as the multinomial or binomial) are not valid. Nonetheless, some basic unit weight of sample must be defined. In traditional cluster sampling theory, a balance is achieved between the within-cluster and between-cluster components of the total variability of an estimate. If the cluster (i.e., in this context, a sample of given weight) is too small, then the between-cluster variability will be greater than the within-cluster variability and will result in a large sample variability. If the cluster weight is too large, however, the greater will be the time and expense of sampling. Since this is not a linear relationship (i.e., doubling the cluster size will not necessarily double the precision of the estimate), the optimal procedure is to select that cluster size where the precision of the sampling estimate does not significantly improve with cluster size. For raw municipal solid waste, this sample weight has been found to be between 200 and 300 lbs. For processed waste streams, on the other hand, it has been found that particle size distributions are adequately described by functions based upon the exponential distribution, such as the Rosin-Rammler equation. Such equations are also fully described in this study.

COMPONENT ESTIMATION

When it is desired to place confidence intervals about the estimates made in the sample estimation process, traditionally the distribution of either the population or of the population parameter estimated is assumed to follow a specific classical probability distribution; typically, the normal distribution is assumed. In the sample selection process, similar assumptions are made when determining the number of samples to be taken. The method is applied in an iterative, trial-and-error procedure.

Although such assumptions are justifiable in the estimation of solid waste quantity, such is not the case in estimating solid waste composition. For one thing, component fractions are bounded, i.e., there are no components in solid waste that are present in fractions less than zero or greater than one. These boundaries are generally located close to the means of their distributions. Thus, solid waste component distributions are, at the very least, positively-skewed (i.e., skewed to the right) and, at worst, are J-shaped. Nor does reliance on the Central Limit Theorem of statistics help much, since even averages of component fractions do not approach normality quickly, at least not within an economically feasible number of samples. Distributions of component averages still tend to be positively-skewed. This characteristic precludes the rote application of the traditional statistical formulas for either the estimation of sample size or the construction of confidence intervals. Although transformations can be used to construct the proper asymmetric confidence intervals after the sample data is obtained, these are of little help for estimating sample size before the sample is taken. A knowledge of the effect of positive skewness on the actual level of significance of a confidence interval, however, can be of help in determining the number of samples to take.

Since the rationale behind using the Central Limit Theorem is to permit the use of t-statistics to construct confidence intervals about the estimation of the percentage of any component in the waste stream, an appropriate measure of the ability to meet the normality requirements is the fraction of confidence intervals that actually contain the true mean at a given level of significance. For example, Monte Carlo simulations have shown that, given an average of size 10, if a confidence interval at a nominal significance level of alpha-nominal = .05 were constructed about the mean, the actual significance level would be alpha-actual = .104. In other words, instead of a 95% confidence interval, we would actually be constructing an 89.6% confidence interval. As the size of the average gets larger, the discrepancy gets smaller. For example, at a nominal significance level of alpha-nominal = .05 and an average of size 50, the actual significance level is alpha-actual = .138. For moderately positively-skewed distributions, such as ferrous metals, these discrepancies are very much smaller, even for very small sizes of the average. From the data developed in this study, however, equations have been obtained that relate alpha-nominal and alpha-actual.

Although the calculations dictated by these protocols - including those for quantity, composition, and sampling size - are arithmetically tedious, a computer program (designed to be run on personal computers with modest capabilities) has been developed to carry out these tasks. The program, called PROTOCOL, also contains routines that check input data for errors in coding, and an editor for preparing and modifying input data files.

CONCLUSIONS

Efficient and statistically sound sampling protocols for estimating the quantity and composition of solid waste over a stated period of time in a given location, such as a landfill site or at a specific point in an industrial or commercial process, are essential to the design of resource recovery systems and waste minimization programs, and to the estimation of the life of landfills and the pollution burden on the land posed by the generation of solid wastes. The theory developed in this study takes a significantly different approach over the more traditional sampling plans, resulting in lower costs and more accurate and precise estimates of these critical entities. A computer program, called PROTOCOL and designed to be run on personal computers with modest capabilities, has also been developed to do the calculations required.

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PRICE INFORMATION AND THE HAZARDOUS WASTE REMEDIATION INDUSTRY

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INTRODUCTION

The rapid growth of the hazardous waste remediation industry during the past 10 years has resulted in the development of market imperfections which have inhibited it's efficient operation. Through the use of the classical economic paradigm, this presentation will analyze one aspect of this market, the role of price information. The prescriptions which are offered leave the hope that greater efficiencies can be obtained through systematic efforts to gain consensus to the meaning of price information.

METHODOLOGY

This economic inquiry starts with a problem that forms the foundation for all subsequent analysis; the scarcity problem. One side of the basic economic problem is rooted in the unlimited wants and needs of individuals. The other side reflects the limited availability of land, labor, capital, and time. Together, the two problems create the condition of scarcity. Modern economic theory is focused on examining the mechanisms employed by individuals and society to cope with the scarcity problem.

Every society has faced the scarcity problem. Our society has relied on markets to help us reach consensus on the allocation of society's scarce resources. Markets are dynamic mechanisms for transmitting information on scarcity; this information comes in the form of prices. Trade occurs when both buyer and seller benefit. In any market, price is a reflection of a mutual agreement between demand and supply forces regarding scarcity. In efficient markets, the latest price information reaches others almost instantaneously. The key idea is that markets produce prices which give information on scarcity.

THE MARKET

It's natural for buyers and sellers to focus on that part of the scarcity problem which they are most familiar with. Suppose a problem site contains soils and groundwater contaminated with PCBs. Demand is likely to be driven by the public's understanding of the hazards involved and their outrage over the problem. This manifests itself in a desire for a minimal impact, 0-residual, 0-emission, destructive remediation. On the other side of the market are vendors prepared to provide various technologies as a solution to the problem. Though both sides are reacting to the same reality, buyers and sellers see the problem differently, and tend to act accordingly.

It has become a common practice within the remediation industry to discuss prices in a form of shorthand. This shorthand expression of price sets forth the terms of trade in dollars per quantity of waste matrix treated (i.e., $/ton, $/gal, $/cu yd). Our problem begins here. The more distant one is from negotiations for the procurement of remediation services (based on site specific conditions), the more likely it is that this shorthand price information will become part of the basis for decision making. While a shorthand method of conveying price information may be convenient, its use assumes that buyers and sellers are in general agreement regarding the services rendered for the price quoted. Herein lies the source of a major market imperfection.

During the early stages of a site remediation (when various technology solution are under consideration) buyers and sellers begin to discuss the price in shorthand terms. Unfortunately, those on the buying side of the market tend to infer that the terms of trade cover a greater range of activities than sellers expect to deliver. At the present time, there is no common definition regarding the activities which are reflected within the "dollar per unit treated" price quotes. The time has come to adopt a more precise price definition.

THE SITE PROGRAM'S EXPERIENCE

A study of Applications Analysis Reports prepared under the auspices of the USEPA's Superfund Innovative Technology Evaluation (SITE) Program provides some interesting insights into the problem of ill-defined prices. Before examining that analysis, a brief review of the SITE Program and it's efforts to report on technology costs is in order.

The SITE Program was established by Congress through the passage of the 1986 Superfund Amendments and Reauthorization Act (SARA). The goal of the SITE Program is to assist Superfund decision makers through the creation of reliable performance and cost data for unique and commercially available hazardous waste destruction and treatment technologies. The special nature of this public/private sector interaction suggested the need to establish a protocol which would guide analysts as they try to project the costs of new hazardous waste treatment technologies. Four problems were identified which would limit the ability of a SITE demonstration to generate realistic cost data:

1) Each field demonstration is a mix of unique factors.
2) The research and development aspects of each demonstration will impact the observed costs.
3) Each developer is a profit maximizer operating within a competitive marketplace.
4) The SITE Program creates unique interactions between public and private sector forces.

With the potential for dozens of demonstrations to be conducted over the life of the SITE Program, the large number of independent variables involved with each demonstration made the usefulness of a single, rigid protocol suspect. Instead, general guidelines were established that would aid in the development of each cost projections. The idea was to create a high degree of uniformity among all the SITE cost projections while allowing the unique conditions of each demonstration to dictate how each projection would be built.

The most important step in this process was to establish a set of cost categories which would serve as a common framework for all base-case cost projections. These 12 categories, listed in Table 1, were an early attempt to provide some structure to the terms of trade with in this industry.

TABLE 1. COST CATEGORIES USED BY THE SITE PROGRAM

1. Site Preparation
2. Permitting & Regulatory Requirements
3. Capital Equipment
4. Start-Up
5. Labor
6. Consumables & Supplies
7. Utilities
8. Effluent Treatment & Disposal
9. Residuals/Waste Shipping & Handling
10. Analytical Services
11. Maintenance & Modifications
12. Demobilization

Under ideal conditions, a demonstration would generate enough information regarding each cost category to build a complete "start to finish" cost projection. In reality, however, a lot of cost data is unavailable. Thus, when assigning costs, the analyst is instructed to include only those activities for which solid or defensible cost data is available. The analyst is instructed not to list costs for those categories where there is limited or incomplete cost data. An empty category is not discarded, but explicitly labeled as empty. This approach provides the reader with a clear and explicit definition of the activities which are included for each cost projection.

In addition to the establishment of the 12 cost categories, four other rules were set forth to guide the conduct of each SITE cost analysis. In summary, the five cost projection guidelines are as follows:

1) Place each cost analysis within a common framework of 12 cost categories.
2) Present the cost projection as "Order-of-Magnitude" estimates (+50% and -30%).
3) Provide full disclosure of all assumptions and calculations used in the analysis.
4) Identify key operating parameters likely to have significant cost implications beyond normal operations.
5) Offer developers with the opportunity to present their own cost analysis.

While no methodology can insure that projected costs are delivered with the same degree of precision that engineering or chemical data is, these simple protocols go a long way to insuring a consistent approach.

THE ANALYSIS

In an effort to characterize the wide degree of variation found within the terms of trade, a review of 23 published SITE Applications Analysis Reports was conducted. The economic analysis found within each Applications Analysis Report was reviewed and their contents cataloged.

It was noted that costs projections were reduced to a simple dollar per unit treated cost quote in 87% of the reports. This shorthand cost data was typically reported in both the Executive Summary (where assumptions supporting the costs were usually ignored) and in the underlying cost analysis (where the assumption were explicitly stated).

The frequency with which each of the 12 cost categories were covered within the 23 reports was computed and is presented in Table 2.

TABLE 2. COST CATEGORIES, AND THE FREQUENCY OF USE IN APPLICATION REPORTS

A.	Utilities	100%
B.	Labor	100%
C.	Capital Equipment	100%
D.	Consumables & Supplies	96%
E.	Start-Up	91%
F.	Maintenance & Modifications	78%
G.	Site Preparation	74%
H.	Demobilization	74%
I.	Analytical Services	65%
J.	Permitting & Regulatory Req.	48%
K.	Residuals/Waste Shipping	43%
L.	Effluent Treatment	39%

CONCLUSIONS

Basic disagreement between buyers and sellers with regard to the meaning of price information has created a situation where the search for cost efficient remediation solutions is inhibited. In the short term, the practice of screening technologies on the basis of shorthand price data will likely lead to situations where unexpected and significant cost escalations occur. In the long run, reliance on shorthand cost data will provide markets with imperfect scarcity information, with the outcome being an inefficient allocation of society's scarce resources.

USING FOURIER TRANSFORM INFRA-RED SPECTROSCOPY (FT-IR) TO MONITOR THE PROGRESS OF PLANT BASED BIOREMEDIATION EFFORTS.

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INTRODUCTION

Bioremediation usually provides a less costly means of correction for contaminant problems than does a fully engineered approach (1). Frequently, intrinsic bioremediation is effective and even less costly, but it may be more time-consuming. We have sought to develop a plant based bioremediation in which root exudates provided by plants augment the intrinsic remediation ability of a soil system by enhancing microbial populations. Plants, through their use of water may also stimulate the remediation process by drawing contaminated water into the aerobic vadose zone from the typically anaerobic ground water.

Monitoring is a major cost associated with any remediation effort. We have developed an open path/ long path system of Fourier Transform Infrared Spectroscopy (FT-IR) to use in monitoring gas phase concentrations of volatile compounds. All organic compounds and many other volatiles of interest, including CO_2, SO_2, and CO, have useful infrared signatures. A commercially available FTIR instrument has been used to monitor the gas phase above plants growing in the presence of dissolved organic contaminants including toluene (2). The present work describes extension of that study to trichloroethylene (TCE) and trichloroethane (TCA) in ground water, gas phase and plant tissue.

METHODOLOGY

Design and construction of the plant treatment system was previously described (2). Briefly, the plant growth chamber consists of two identical halves each having a channel 10 cm wide, 35 cm deep and 1.8 m long folded in a U shape for convenience. Fluorescent lights 40 cm above the ground surface provide illumination for growth of alfalfa planted at 10 cm intervals along the channel. An aluminum and glass enclosure 26 cm high allows sealing of the gas phase above the plants to monitor gas phase concentrations of volatiles. Ground water is maintained to a depth of about 10 cm from the bottom, giving a 25 cm vadose zone. Compounds of interest are introduced into the water source at the desired concentration. In earlier experiments (2) toluene and liquified phenol were added at levels of 500 μL/ L water (2). For these experiments TCE was added at 200 μL/L and TCA was added at 50 μL/L. Four sampling wells, spaced at nearly equal intervals (33 and 66 cm from the ends) in each channel, allow monitoring of the concentration of substances in the ground water.

Use of the MIDAC FT-IR to monitor gas phase concentrations of volatile organics was previously described (2). Light from a glowing source enters from one side of the upper gas phase enclosure through a KBr window. It is then reflected from a mirror set at c. 45° to the end of the chamber, from which it is reflected back to the 45° mirror and out through another KBr window close to the entrance. The internal pathlength is 2.44 m while the external path is about 0.6 m. Changes in gas phase concentrations of materials in the external path between collected spectra affect the observed spectra but have not presented difficulties except in precision determination of CO_2 concentration.

Concentrations of volatile organic compounds such as CH_4, TCE and TCA in the ground water have been monitored at frequent intervals by head space gas analysis using a gas chromatograph. Peak positions relative to known standards were used for identification. Standards used are indicated below. They have also been measured with good sensitivity by use of the FT-IR system. A 0.5 m pathlength cell closed with KBr windows and having an internal volume of 697 mL has been used for calibration and headspace gas analysis. The sample to be analyzed (3 mL of ground water) is collected with a syringe and nylon tubing as for gas chromatography. It is placed into a vial (c. 10 mL), sealed with a reacti-vial cap (Pierce Chemical Co.) and then shaken to equilibrate the head space. The gas cell is evacuated. Then the head space is transferred to the gas cell by opening a stopcock which has an attached needle inserted through the closure of the reacti-vial. About 99% of the gas phase should be transferred in this way. In this instrumental configuration the open path length is about 0.3 m while the internal path length is 0.5 m. Only water, ammonia and CO_2 concentrations in the external path have affected calibration measurements. None of these are compounds of interest for study of ground water in these experiments.

To measure concentration of volatile materials in aboveground plant tissues, the plants were cut at 5 cm above the soil surface and quickly transferred to a glass jar which was then sealed. The lid was modified by addition of a fitting with a rubber gas chromatograph septum to allow transfer of the gas phase from the bottle to the FT-IR cell. Typical plant samples contained 10-12 mL of water.

Limits of detection from compounds of interest were determined by calibrating the 0.5 m cell with known amounts of individual compounds. In each case four manometrically measured partial pressures of the pure compound were diluted in N_2 gas. In each case Beer's law was obeyed over the concentration range examined - up to 2.4×10^{-5} M (mol substance/ L gas). The limit of detection, estimated as 3 times the peak to peak noise in the spectral region of interest was below 10^{-6} M. Compounds calibrated included 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1-dichloroethane, 1,2-dichloroethane, trichloroethene, 1,2-dichloroethene, *cis*-1,2-dichloroethene, *trans*-1,2-dichloroethene, methane and carbon dioxide. Values for vinyl chloride were obtained from earlier studies with a 0.05 m cell.

RESULTS

The initial planting of alfalfa was done in June 1992 and plants have been maintained since that time with harvesting of most of the aboveground biomass at about monthly intervals. Plants in one half of the chamber were exposed to c. 500 ppm phenol from June 1992 to May 1993. Following a washout of phenol, TCE and TCA were introduced at the end of June 1993. Most experiments described here were conducted in September and October of 1993 by which time the levels of TCE and TCA had reached a steady state of introduction and degradation. The other half chamber was used for toluene feeding and then a conservative tracer, KBr, was introduced to determine the dispersion characteristics of the soil system. Comparison of elution rates indicates that there is significant adsorption to the soil, even though it is low in organic matter (c. 1%). Significant degradation of phenol in the ground water was observed (2, unpubl obs) while toluene concentration in ground water was unaltered but a mass balance required significant loss of toluene from the whole system. Outflow of water was from 10-30% of input, while the remainder was lost through evapotranspiration. Toluene was below the limit of detection in the gas phase above the plants (2), indicating that 70-90% of the input must have been degraded.

Treatment of the soil with phenol may have enhanced the population of bacteria containing specific hydroxylase enzyme able to metabolize TCE (1). Degradation of TCA is generally considered to happen only anaerobically; it is a rather recalcitrant compound (1). Ground water

head space gas analysis indicated that CH_4 was present in the ground water at the 3rd and 4th sampling wells. Chloride ion concentration was also increased in the water at the outflow. This indicates that some TCE or possibly TCA, was being degraded anaerobically to some extent. A further portion of the TCE may have been degraded in the vadose zone. To determine the extent of degradation of TCE relative to TCA, the gas phase above the plants was monitored by FT-IR. Concentrations of both were also measured in the ground water by head space gas analysis using FT-IR. Some typical results for ground water are shown in Figure 1.

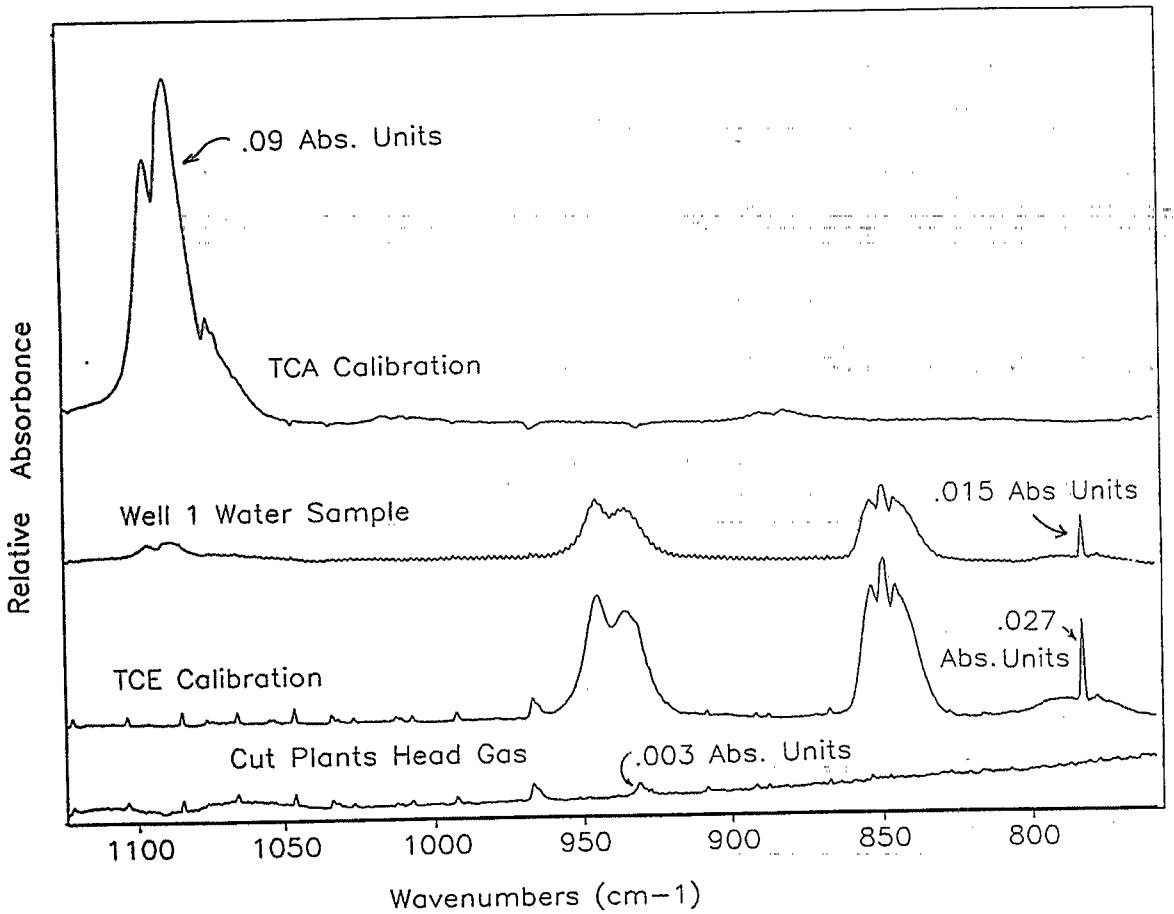

Figure 1

Calibration spectra for TCE and TCA were obtained at 6 x 10^{-6} M. Peak heights (absorbances) of a few peaks are indicated for comparison purposes. Water from well # 1, sampled as described above, yielded half the calibration amount of TCE, about 5-10x above the limit of detection for compound in this experiment. Recovery was lower than predicted on the basis of input and detailed studies of mass balance continue. Levels of TCA are, as expected from the input, 4 fold lower than those of TCE. The spectrum of the head space gas of cut plants showed a limit of detection of 1.2 x 10^{-7} for TCE, TCA and CH_4. The limit of detection corresponds to an absorbance of less than 0.003 as may be clearly seen in this spectrum. Molar absorptivities of the dichloro compounds are several fold lower than TCE or TCA, yielding correspondingly higher limits of detection. A search of the region from 700-1400 cm^{-1} for diagnostic features of all of the dichloro compounds referred to in Methodology gave no indication of their presence above the limit of detection. Gas chromatography studies of ground water samples taken on the same dates indicated that the various partially dechlorinated ethanes and

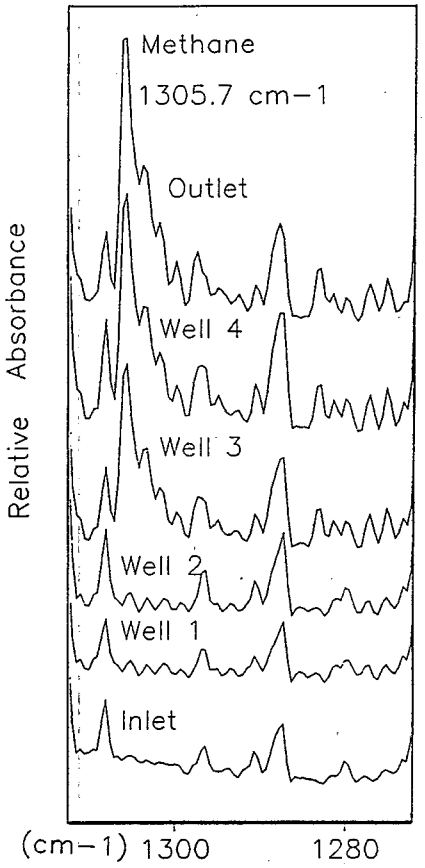

Figure 2

ethenes could not constitute more than a few percent of the observed concentrations of TCE and TCA.

In the ground water both TCE and TCA concentrations decreased by about 1/3 from inlet to outlet. Calculated concentrations based on input volumes should have been 2.23 and 0.5 mM respectively. Measurable levels of methane were found in the ground water only in the latter half of the flow path of the chamber (Figure 2). Methane levels in the gas phase from ground water samples were calculated to be 2.75, 3.72 and 4.8 x 10^{-6} M for wells 3,4 and outlet respectively. This corresponds to 1.2 mM in the ground water sample. Chloride ion analysis indicated only about 0.7 mM chloride, suggesting that some methane may have come from materials other than TCE and TCA. Complete conversion of 1/3 of both TCE and TCA to methane should have yielded about 1.8 mM methane and 2.& mM chloride in the water, assuming that none of either was transferred to the vadose zone prior to exiting the chamber.

Studies of volatiles accumulating in the gas phase above the well grown plants, or with the plants cut to 5 cm showed significant accumulation of TCA but not of TCE within less than one hour. The detection limits for both compounds are quite similar so that failure to detect TCE indicates that it must have been metabolized in the vadose zone. In the ground water, concentrations of the two compounds were proportional (*c. 1:4*) as expected from the input concentration ratio.

CONCLUSIONS

A FT-IR system has been successfully applied to determination of contaminant levels in the gas phase, ground water and plant tissues. It provides rapid analysis from small amounts of material and is capable of detecting both the initial contaminant and its volatile products if they are produced as a significant fraction of the input material. The system is mobile and may easily be transported to locations where remediation efforts are underway.

REFERENCES

1. Thomas, J.M. and Ward, C.H. In situ biorestoration of organic contaminants in the subsurface. Environ. Sci. Technol. 23: 760-766, 1989

2. Davis, L.C., Chaffin, C., Muralidharan, N., Visser, V.P., Fateley, W.G., Erickson, L.E., and Hammaker, R.M. Monitoring the beneficial effects of plants in bioremediation of volatile organic compounds In: L.E. Erickson, D. Tillison, S.C. Grant and J.P. McDonald (eds.), Proceedings of the 8th Annual Conference on Hazardous Waste Research . Engineering Extension Service, Kansas State University, Manhattan, KS. 1993. pp 236-249,

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FIELD SCALE EVALUATION OF GRASS-ENHANCED BIOREMEDIATION OF PAH CONTAMINATED SOILS

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INTRODUCTION

The toxicity and carcinogenicity of polynuclear aromatic hydrocarbons (PAH) gives rise to concern over PAH contaminated soils. Two and three ring PAH compounds are biodegradable and can serve as growth substrate for microorganisms. Higher molecular weight PAH compounds may be cometabolized by soil microorganisms. The enhancement of biodegradation of pesticides, and other environmental contaminants, in the rhizosphere suggests that similar acceleration of the biodegradation of PAHs may occur in this environment.

In situ degradation processes in low permeability, clay soils are often slow. This may be due to the slow flux of nutrients and electron acceptors through the soil resulting in limited microbial respiratory activities. PAHs are generally resistant to biodegradation under methanogenic or sulfate reducing conditions in contaminated subsurface environments. Maintaining a well aerated condition in soil with low permeability is a challenge.

While PAH degradation and humification may take considerable time, turf grasses provide short term benefits by reducing the risk posed to human health and the environment. Dense turf grasses serves as a botanical cap to prevent exposure to soil born contaminants by direct ingestion, inhalation, and skin contact of soil dust. Turf grasses also reduce potential contaminant migration through surface runoff and infiltration to ground water resources.

Union Carbide and Utah State University jointly initiated research on grass enhanced bioremediation of PAH contaminated soil in 1989. A preliminary laboratory study showed that high molecular weight PAHs in soil can be degraded in the presence of prairie grasses and cow manure additions. The study also indicated a significant reduction of water infiltration through the grass root zone. Subsequent laboratory mass-balance experiments, using radio labeled compounds, indicated that mineralization rates of phenanthrene and pentachlorophenol were significantly enhanced in the presence of prairie grasses. Enhancement of the volatilization rate of naphthalene in the presence of prairie grasses suggested that the roots improved soil aeration. A seed germination study indicated that prairie grasses were tolerant to the PAH contamination and may survive in clay soil with significant levels of PAH, oil and grease. It was hypothesized that a deep, fibrous root system of prairie grasses may improve aeration in soil and broaden the spectrum of degradative capability in the rhizosphere and the organic exudates from roots may induce microbial cometabolism of high molecular weight PAH. Based on these results, a field pilot scale study was started in 1992 to test this hypothesis. The primary objective of the pilot study is to evaluate the enhancement of the rate and extent of PAH biodegradation by the establishment of a grass root zone in clay soil in the field environment. Treatment performance is being evaluated by assessing degradation kinetics of PAH compounds.

METHODOLOGY

The field plots were constructed at Union Carbide's Seadrift Plant. Site selection and characterization were based on available information regarding regional hydrogeology, contamination history, background soil sampling and analysis, as well as long term land use planning and safety considerations. The Seadrift Plant is located in Calhoun County, Texas, near the Gulf of Mexico. The test

site is a leveled surface at an elevation of approximately 28 feet (8.5 m) above MSL. The ground water table is approximately 6 feet (1.8 m) below the surface. The top soil contains 50 to 60% clay. The top of the uppermost sandy aquifer is approximately 13 feet (4 m) below the ground surface. The ground water is high in salinity. Local weather records (1951-1980) showed that the mean annual precipitation was 39.5 inches (100.3 cm) and the mean annual lake evaporation was 59 inches (149.9 cm). The annual average daily low and high temperatures were 63 - 78° F (17.2 - 25.6° C). The monthly extremes were 45° F (7.2° C) in January and 91°F (32.8° C) in July and August.

Exploratory soil samples were taken at 1 to 3 ft (30.5 - 91.4 cm) depths below the ground surface from ten candidate locations at the Seadrift Plant. Composite soil samples for each of the locations were analyzed for PAH constituents. The final site was selected due to its representative PAH constituents and concentration levels.

Two plots, each 10 X 20 ft (3.05 X 6.1 m), were constructed for the study. One plot was sodded with 'Prairie' Buffalo grass and the other was kept free of vegetation. Table 1 shows the three-factor factorial experimental design for the plots. They were constructed between the subgrade foundations of an old olefins unit building in Union Carbide's Seadrift Plant. The building had been demolished after the operation was shut down. The soil underneath the building had been contaminated by the process material; mainly pyrolysis gasoline. The contaminants present in the soil are benzene, toluene, and PAHs including naphthalene, fluoranthene, etc. The plots were divided into 10 subplots, each 4 X 5 feet (1.22 X 1.52 m) and a sample core was taken from each of the subplots at each sampling event. The location of the core within the subplot was determined using systematic random methods and a rectangular grid.

Table 1. Experimental design.

Factor	Description	Number
Replicate samples		≤ 10
Vegetation	Plot 1 - Unvegetated control Plot 2 - Vegetated	2
Sample depth	Surficial (0 - 1 ft) Subsurface (1 - 4 ft)	2
Time	4 - 6 month sample intervals	7
Total soil samples		≤ 280

Sampling was designed to assure that enough samples were taken to accurately estimate the variation of the contaminants within each plot while minimizing alteration of the soil environment so that plant growth, soil moisture dynamics, gas exchange, etc., were not interfered with. A limit of less than 1% of the plot surface disturbance by sampling was chosen to protect against these interference. The number of sampling points on each plot was no more than ten in each of the seven sampling events.

Performance evaluation was done by measuring extractable PAH concentration reduction in soil over time and with depth in the testing plots. Soxhlet extractions were done using 1:1 (v:v) methylene chloride:acteone followed by concentration using Kaderna-Danish apparatus. Concentrations of PAH compounds in the extracts were determined using gas chromatography/ion trap (mass spectrometry) detection.

Data analysis indicated that the distribution of PAH concentrations within each of the plots was log-normally distributed. Analysis of variance procedures were, therefore, performed on the log + 1 transformed data. All values reported below the limit of quantitation were assigned the value zero for data analysis purposes.

RESULTS

Concentrations of naphthalene, acenaphthylene, acenaphthene, phenanthrene, and anthracene were routinely monitored in soil samples from the plots. All of the other 16 priority pollutant PAH compounds were not found in environmentally significant concentrations in the initial samples. In general, only naphthalene, acenaphthylene, and phenanthrene were found in quantifiable concentrations frequently enough to allow reliable use of normal statistics in the data analysis. For this reason, only data for these three compounds will be presented. Average phenanthrene concentration decreased significantly in both the vegetated and unvegetated plots. Shallow sample concentrations in the vegetated plot tended to be lower than in deep samples. Acenaphthylene also decreased in both plots over time and was present in higher concentrations in unvegetated shallow soil than in vegetated shallow soil. Naphthalene concentrations have changed little over the experiment to date. As with phenanthrene and acenaphthylene, naphthalene concentrations tended to be higher in the unvegetated shallow soil than in the vegetated shallow soil.

CONCLUSIONS

The experiment described is still in progress and the data presented here must be considered to be preliminary and the interpretation of the data is subject to revision. To date, it appears that PAH degradation in the Seadrift plots is slow. Surprisingly, naphthalene degradation kinetics appear to be particularly slow. There is some evidence that Buffalo grass sod planting and establishment has enhanced degradation in the near surface soil.

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ISOLATION OF POLLUTANTS USING A BIOBARRIER TECHNOLOGY

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INTRODUCTION

For several decades Microbiologists have known that bacteria can produce several times their own weight in slimey exopolysaccharides that can readily plug porous media such as sand filters. This characteristic of bacteria has militated against their use as agents of bioremediation, because it limits their mobility through porous media, but it has led to numerous suggestions that they could be used selectively to plug the high permeability zones that mediate water breakthrough in secondary oil recovery by water flooding. We have examined the passage of bacteria through porous media (1.6 darcy: 27 μm pore throats) and we have found very shallow penetration and almost complete plugging by these organisms (1). Because these bacterial plugs were too shallow (< 1 cm) to be useful, and because they could not be positioned deep within a porous medium, they have not been used in selective plugging.

A decade previously Morita's group had discovered (2) that marine bacteria reacted to starvation by producing ultramicrobacteria (UMB). These UMB are very small (±0.3 μm in diameter) when compared to the vegetative cells from which they were derived (± 1.0 μm) and they are metabolically dormant and produce only very small amounts of exopolysaccharide (EPS). We reasoned that UMB would probably penetrate porous media more readily than vegetative cells and we know from the literature (2) that they would return to their full vegetative size and produce large amounts of EPS if they were provided with nutrients at some location within these porous media. It is now abundantly clear that the physiological state of bacteria has a profound effect on their passage through porous media and that the successful exploitation of this scientific fact will lie at the heart of successful technologies in oil recovery and in bioremediation.

METHODOLOGY

UMB are produced from natural strains of bacteria recovered from produced groundwater by starvation for 60 days in a high salts medium deficient in organic carbon nutrients (3). The starvation process is monitored by light microscopy and the final suspension of UMB, which can readily be produced at concentrations of 5×10^8 cells/ml, is centrifuged at 100,000 xg for 15 minutes and washed several times in PBS to produce a uniform suspension of small dormant cells. The nutrient solution

used to resuscitate these UMB in situ in the porous media is a solution of sodium citrate containing several salts.

The physical simulator used in these studies is described in Figure 1 and it consists of a sand-filled drum, maintained under simulated overburden pressure, in which the UMB and the nutrient solution can be injected sequentially at a single point and detected at 8 different probe locations to detect their radial distribution. In this experimental design the UMB were injected until they could be detected at all 8 sampling probes and then the nutrient solution was injected at intervals while we monitored the injection pressure to detect plugging of the porous medium. At the end of each experiment, typically 21-40 days, the physical simulator was dismantled and samples of the sand were taken at carefully selected locations to be analyzed for their content of bacteria and EPS by chemical and morphological methods (3).

RESULTS

When one pore volume (PV) of a 1×10^6 cells/ml suspension of UMB was injected into the physical simulator sandpack, which had an effective permeability of 1.3 darcys, these small dormant cells had reached even the most distant sampling probe within 105 minutes (Table 1) after injection. The number of these UMB at each sampling location varied from 1.2 to 3.6×10^5 at these locations. These data attest to the ability of UMB to penetrate this porous medium.

When the nutrient solution was injected to initiate the resuscitation of these UMB in situ in the physical simulator the number of resuscitated vegetative cells/ml of pore fluid reached at least 1.2×10^7 cells/ml by day 5 and at least 2.3×10^8 cells/ml by day 18. The size of these vegetative cells (> 1.0 μm) was confirmed directly by light microscopy. The injection pressure of the physical simulator gradually increased from an initial level of 8 kPa to > 100 kPa as the UMB were resuscitated by nutrients in situ. When the experiment was terminated sand samples were taken from various locations, as the physical simulator was dismantled, and direct microbiological and chemical measurement of the numbers of bacteria and the μg of EPS per gram of sand clearly indicated that the porous sand matrix of the physical simulator had been uniformly and completely filled by bacterial cells and their EPS. Scanning Electron Microscopy (SEM) of the clean sandpack and the sandpack at the end of the nutrient-stimulated UMB plugging experiment (Figure 2) clearly shows the complete occlusion of the pore spaces by vegetative bacterial cells and their slimey EPS. These data attest to the ability of UMB to respond to nutrient stimulation by replicating and by producing EPS to effect complete plugging of this porous medium.

CONCLUSIONS

We have previously presented data to establish that vegetative bacteria are capable of plugging porous media but that the resultant plug is very shallow (1) because of biofilm formation on the closest available surfaces (4). In this paper, and

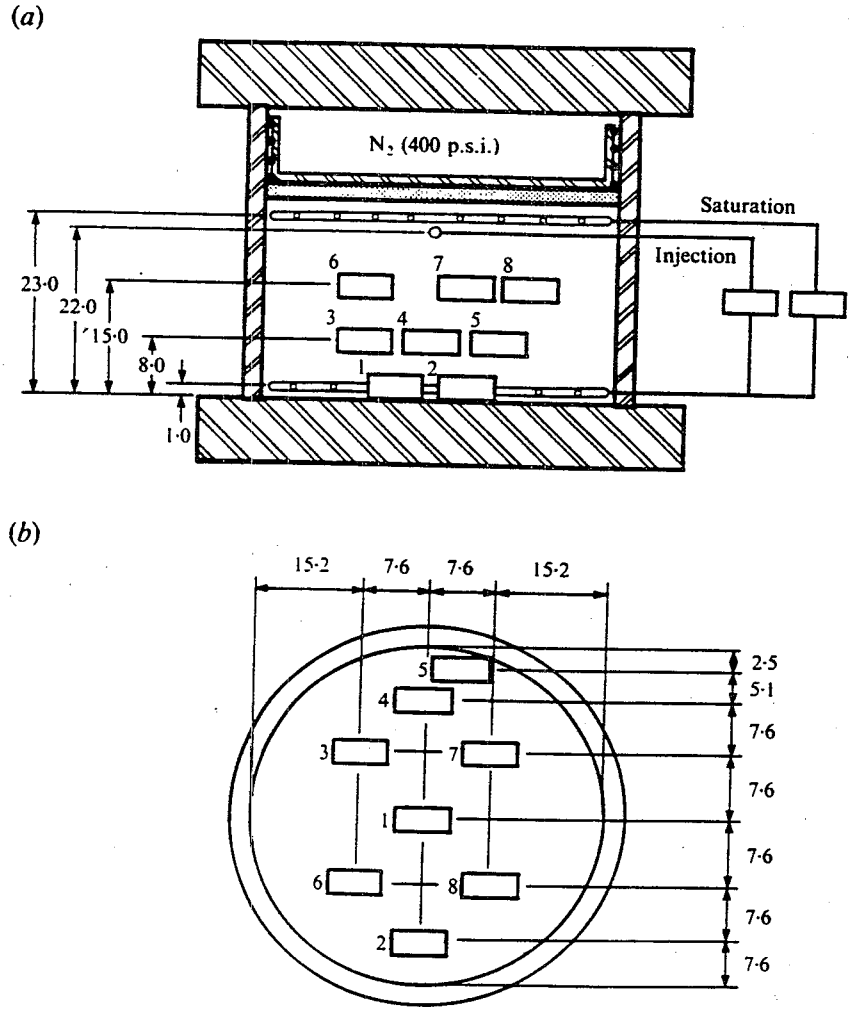

Figure 1. The design of the three-dimensional sandpack 45 cm in diameter by 38 cm in length, showing the location of the eight probes (1-8) within the sandpack viewed (a) from above and (b) as a cross-section. All dimensions are given in cm.

Table 1. Penetration of umb through the sandpack following their injection in one pore volume.

Probe no.	Viable cell numbers (c.f.u. ml^{-1}) after (min):					
	5	15	45	75	105*	165† (1·5 PV)
1	NS	NS	NS	$7{\cdot}3 \times 10^4$	$1{\cdot}5 \times 10^5$	$4{\cdot}5 \times 10^5$
2	NS	NS	$2{\cdot}5 \times 10^4$	$6{\cdot}3 \times 10^4$	$1{\cdot}3 \times 10^5$	$5{\cdot}0 \times 10^5$
3	NS	NS	NS	$9{\cdot}1 \times 10^4$	$1{\cdot}2 \times 10^5$	$2{\cdot}7 \times 10^5$
4	NS	$1{\cdot}3 \times 10^4$	$1{\cdot}5 \times 10^4$	$5{\cdot}6 \times 10^4$	$1{\cdot}5 \times 10^5$	$1{\cdot}8 \times 10^5$
5	NS	NS	NS	$1{\cdot}2 \times 10^4$	$1{\cdot}5 \times 10^4$	$6{\cdot}5 \times 10^5$
6	$2{\cdot}8 \times 10^4$	$1{\cdot}3 \times 10^5$	$3{\cdot}2 \times 10^5$	$2{\cdot}2 \times 10^5$	$1{\cdot}5 \times 10^5$	$6{\cdot}5 \times 10^5$
7	$3{\cdot}1 \times 10^4$	$9{\cdot}1 \times 10^4$	$1{\cdot}9 \times 10^5$	$2{\cdot}0 \times 10^5$	$2{\cdot}1 \times 10^5$	$7{\cdot}0 \times 10^5$
8	$2{\cdot}0 \times 10^4$	$8{\cdot}1 \times 10^4$	$1{\cdot}9 \times 10^5$	$2{\cdot}5 \times 10^5$	$3{\cdot}6 \times 10^5$	$4{\cdot}0 \times 10^5$

NS, Not sampled.

* After injection of 1 PV, UMB were evenly distributed throughout the sandpack. Mean = $1{\cdot}78 \times 10^5$ c.f.u. ml^{-1}, SD = 0·78.

† After injection of 1·5 PV, UMB were evenly distributed throughout the sandpack. Mean = $4{\cdot}75 \times 10^5$ c.f.u. ml^{-1}, SD = 1·88.

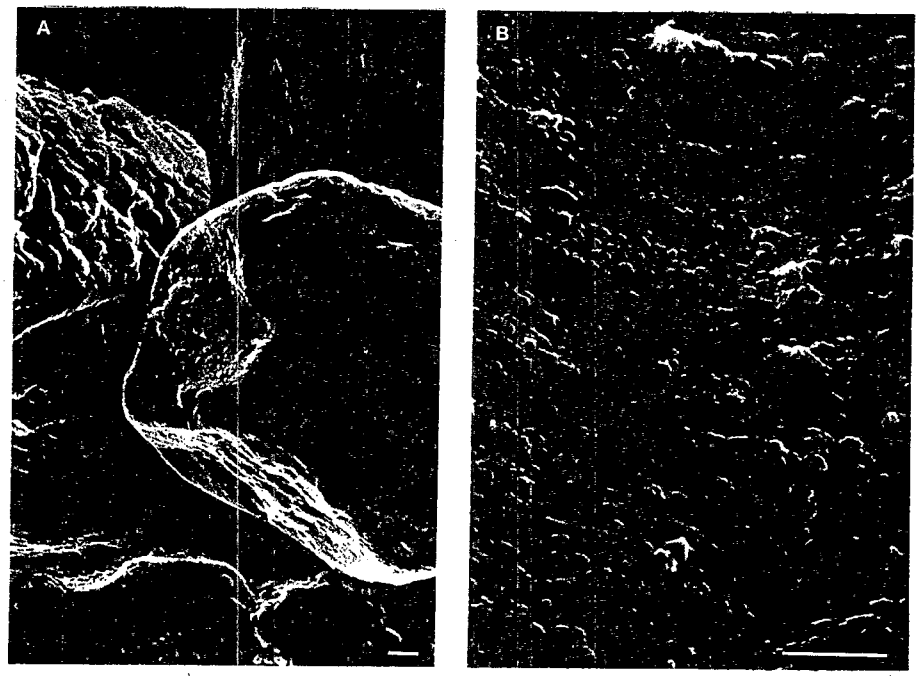

Figure 2. Scanning electron microscopy showing empty pore spaces in a clean sandpack (A) and pore spaces completely occluded by vegetative bacteria and EPS in a sandpack plugged by injection of umb followed by nutrient stimulation (B). The bar indicates 5μm.

in previous publications (5, 6 and 7), we have established that most bacteria can be starved to produce UMB which penetrate readily through porous media > 110 millidarcies in permeability and can then be resuscitated to plug these porous media by cell proliferation and by EPS production.

The UMB deep plugging technology, which was developed for the Alberta Oilsands Technology and Research Authority and is protected by US patent #4,800,959, was initially developed for the selective plugging of permeable breakthrough zones in secondary oil recovery by waterflooding. In this area of application this technology has been tested extensively in the laboratory and is currently in the early stages of application in the fields in Alberta and Saskatchewan. The UMB plugging technology has also been used, in the environmental area, to produce a 4-6 inch deep zone of bacterial growth and EPS production to seal mine tailings so that oxygen cannot penetrate and react with pyrite to initiate acid mine drainage (8). However, the area of application of this technology that is of paramount interest in environmental research is in the isolation of organic and metallic pollutants in the subsurface environment.

It is clear, from these data, that the UMB technology can be used to position deep and effective biobarriers for the containment of pollutants in the subsurface environment. Specifically, bacterial biobarriers can be placed to prevent the movement of pollutants from underground plumes to sensitive ecosystems such as streams and lakes. These bacterial biobarriers are especially useful because they block groundwater flow and contain elements (bacterial cells and EPS) that can potentially degrade organic pollutants and bind metallic ions. Bacterial biobarriers are superior to alternate technologies, such as grout curtains, in that they are very economical and in that they bind intimately to underlying bedrock and do not allow groundwater seepage at the sand/rock interface. The UMB biobarrier technology has already been pilot tested at the mesoscale level at the National Hydrology Institute in Canada and it has been shown to produce a barrier that is elastic, long lived, and 99% efficient in reducing permeability and controlling groundwater flow. We suggest that this technology, which involves the drilling of a series of shallow wells from which UMB and nutrients are sequentially injected, can be used to prevent the passage of underground pollutants into sensitive ecosystems. We plant to inject UMB into these shallow wells and to then inject sufficient amounts of nutrient to produce overlapping columns of soil in which the pore spaces are virtually sealed by bacterial proliferation and EPS production. We are confident that the resultant bacterial biobarriers will be very effective in isolating a wide variety of pollutants in the underground environment. Following their effective isolation by this UMB technology it is clear that organic pollutants will be biodegraded by the injection of degradative bacteria that will be manipulated in the opposite way in order to maximize penetration and minimize EPS production.

The UMB biobarrier technology is currently being pilot tested in a macroscale facility and we expect that it will be ready for field trials within the next 18 months.

REFERENCES

1. Shaw, J.A., Bramhill, B., Wardlaw, N.C., and Costerton, J.W. Bacterial fouling in a model rock core system. Applied and Environmental Microbiology 50: 693-701, 1985.

2. Novitsky, J.A. and Morita, R.Y. Morphological characterization of small cells resulting from nutrient starvation of a psychrophilic marine vibrio. Applied and Environmental Microbiology 32: 617-622, 1976.

3. Cusack, F., Singh, S., McCarthy, C., Grieco, J., de Rocco, M., Nguyen, D., Lappin-Scott, H., and Costerton, J.W. Enhanced oil recovery - three-dimensional sandpack simulation of ultramicrobacteria resuscitation in reservoir formation. Journal of General Microbiology 138: 647-644, 1992.

4. Costerton, J.W., Cheng, K.J., Geesey, G.G., Ladd, T.I., Nickel, J.C., Dasgupta, M., and Marrie, T.J. Bacterial biofilms in nature and disease. Annual Review of Microbiology 42: 435-464, 1987.

5. Lappin-Scott, H.M., Cusack, F.M., MacLeod, F.A., and Costerton, J.W. Nutrient resuscitation and growth of starved cells in sandstone cores - a novel approach to enhanced oil recovery. Applied and Environmental Microbiology 54: 1373-1382, 1988a.

6. Lappin-Scott, H.M., Cusack, F.M., MacLeod, F.A., and Costerton, J.W. Starvation and resuscitation of Klebsiella pneumoniae isolated from oil well waters. Journal of Applied Bacteriology 64: 541-549, 1988b.

7. MacLeod, F.A., Lappin-Scott, H.M., and Costerton, J.W. Plugging of a model rock system by using starved bacteria. Applied and Environmental Microbiology 54: 1364-1372, 1988.

8. Blenkinsopp, S.A., Herman, D.C., and Costerton, J.W. The Use of Biofilm Bacteria to Exclude Oxygen from Acidogenic Mine Tailings. In: Proceedings of the Second International Conference on the Abatement of Acidic Drainage, Montreal, 1991. pp. 369-377.

KINETICS OF BIODEGRADATION, SORPTION AND DESORPTION OF PHENOL, SUBSTITUTED PHENOLS AND POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL SLURRY SYSTEMS

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INTRODUCTION

Bioremediation of Superfund soil and sediment sites requires a fundamental understanding of biodegradation kinetics and the physicochemical factors that control the rate of biodegradation. The quantification of biodegradation kinetics provides useful insight into the favorable range of the environmental parameters for the improvement of the microbiological activity, and enhancement of the biodegradation rates of the contaminants in soil, sediments and aquifers and consequently for enhancing the bioremediation of these environments (Tabak *et al.* 1992; Govind *et al.* 1993)[1,5]. Biological treatment systems, especially when used in conjunction with other physical/chemical treatment methods, hold considerable promise for efficient, safe, economical on-site and *in-situ* treatment of toxic wastes.

The main objectives of this research are to quantitate the bioavailability and biodegradation kinetics of organic chemicals in surface and subsurface soil environments, examine the effects of soil matrices and soil conditioning (drying, aging, compacting), and develop a predictive model for biodegradation kinetics applicable to soil systems. The specific objectives of this study are as follows: (1) Evaluate the availability of representative organics in selected soils for biodegradation using biokinetic data; (2) Examine the effects of soil matrices and soil conditioning on the biokinetics; (3) Examine the threshold inhibition of contaminated soils on the microbiota in contaminated soils; and (4) Develop a group contribution predictive biodegradation model for biokinetics in soil systems. This paper highlights biodegradation studies on phenol, several alkyl phenols (p-cresol, 2,4-dimethyl phenol, catechol, hydroquinone, and resorcinol) and selected polycyclic aromatic hydrocarbons (PAHs) (napthalene, phenanthrene, acenapthene, and acenapthylene. The studies incorporate the use of soil microcosms for acclimation of soil microbiota, measurement of respirometric oxygen uptake and carbon dioxide evolution in soil slurry reactors, measurement of carbon dioxide generation rates in shaker-flask systems, and determination of adsorption/desorption equilibria and kinetics. A mathematical model for soil slurry reactors is used to determine the biodegradation kinetics for the selected compounds from the oxygen uptake data. A comprehensive description of experimental data and methodology for the kinetics of biodegradation, adsorption and desorption of the phenolic and PAH compounds was presented and published elsewhere[2-6].

METHODOLOGY

Studies on Soil Microcosm Reactors: The methodology for the establishment of the bench-scale microcosm reactors, including the reactor configuration and supportive equipment description, undisturbed soil cube sampling for

inclusion in the microcosms, procedure for contamination of soil bed with homologous series of organic compounds, description of the application of nutrients and the operation of the microcosm reactors (CO_2 generation analysis and chemical analysis of soil samples and reactor leachates for the parent compound and metabolites) has been fully described elsewhere (Tabak *et al.* 1992; Govind et al., 1993)[1,6]. Each microcosm reactor represents a controlled site, which eventually selects out the acclimated indigenous microbial population in the soil for the contaminating organics. Samples of soil are then taken from the microcosm reactors and used as source of acclimated microbial inoculum for measuring: (1) oxygen uptake respirometrically; (2) carbon dioxide generation kinetics in shaker flask reactors; and (3) for studies with other soil reactor systems. The microcosm reactor units are also being used directly to evaluate the biodegradability of the pollutant organics and to measure their average biodegradation rate in this intact, undisturbed soil bed. One microcosm reactor was spiked with a mixture of phenolic compounds dissolved in deionized distilled water so that the total chemical oxygen demand per kg of soil in the microcosm reactor was 300 mg. Equal concentrations of phenol, resorcinol, catechol, 2,4-dimethyl phenol, cresol and hydroquinone were used in the mixture. The second microcosm reactor was contaminated with 25 ppm each of several polycyclic aromatic hydrocarbons (PAHs) dissolved in a mixture of deionized-distilled water and 0.5% solution of a surfactant, Triton X-100. Control microcosm reactors were uncontaminated soil which was sprayed with an equal volume of deionized-distilled water and soil contaminated with 0.5% solution of surfactant, Triton X-100. Uncontaminated forest soil was selected for all studies presented in this paper.

Respirometric Studies with Soil Slurries: Studies were conducted with soil slurry reactors, wherein the oxygen uptake was monitored respirometrically. The extent of biodegradation and the Monod kinetic parameters for the organic pollutant compounds by soil microbiota were determined from oxygen uptake data. Various concentrations of soil (2, 5, 10%) and compound (50, 100, and 150 mg/L) were mixed with a synthetic medium consisting of inorganic salts, trace elements and either a vitamin solution or solution of yeast extract and stirred in the respirometric reactor flasks. The flasks were connected to the oxygen generation flask and pressure indicator cells of a 12 unit Voith Sapromat B-12, electrolytic respirometer, and the oxygen uptake (consumption) data were generated as oxygen uptake velocity curves. In the case of phenol and alkyl phenols, the compounds were soluble in water. However, for polycyclic aromatic hydrocarbons (PAHs), a large fraction of the compound was insoluble in water. The appropriate PAH chemical was weighed and added as a solid powder to the reactor flask. A more comprehensive description of the procedural steps for the respirometric tests is presented elsewhere (Tabak *et al.* 1992; Govind *et al.* 1993)[1,6].

Kinetic Analysis of Soil Slurry Oxygen Uptake Data: The oxygen uptake data were analyzed by computer simulation techniques and curve fitting methods, using the Monod type equation combined with a nonlinear adsorption isotherm, to determine the soil adsorption parameter, and the biokinetic parameters. The experimental data were analyzed using a mathematical model (equations given below) which include the effect of chemical adsorption / desorption on the soil particles and the adsorption / desorption of the microorganisms from the soil.

$$X_s = K_b X_w \quad (1)$$

$$S_s = K_d S_w^{1/n} \quad (2)$$

$$O_2 = (S_{to} - S_t) - (X_t - X_{to}) - (S_p - S_{po}) \quad (3)$$

$$dX_t/dt = ({}_wX_wS_w)/(K_w + S_w) + {}_{sw}X_s S_s/(K_{sw} + S_s) - (bK_wX_t)/(K_w + S_t) \quad (4)$$

$$dS_t/dt = -(1/y)({}_wX_wS_w)/(K_w + S_w) - (1/y)({}_{sw}X_s S_s/(K_{sw} + S_s)(w/v) \quad (5)$$

$$dS_p/dt = -y_p(dS_t/dt) \quad (6)$$

where subscripts t, s, w and p represent the total, soil, water and degradation products respectively. S is the concentration of compound, X is the concentration of biomass, and S_p is the concentration of the degradation products. ${}_w$, K_w, y and y_p are the Monod equation maximum specific growth rate parameter, Michaelis constant,

biomass yield and product yield coefficient, respectively for the water phase. $_{sw}$, K_{sw} are the Monod equation maximum specific growth rate parameter and Michaelis constant, respectively for the soil phase. b is the biomass decay coefficient, K_d is the soil adsorption isotherm parameter, (1/n) is the soil adsorption intensity coefficient, and Kb is the biomass adsorption parameter. O_2 is the cumulative oxygen uptake. w is the weight of soil in the slurry reactor and v is the total volume of water in the reactor.

Measurement of Carbon Dioxide Evolution Rates: Carbon dioxide generation rates were measured in shaker-flask soil slurry systems and in the electrolytic respirometry soil-slurry reactors in order to assess the rate and extent of biodegradation/mineralization. The CO_2 generation rate measurement serves as an additional tool for quantitating the biofate of these organics in addition to the cumulative respirometric oxygen uptake data from which the biokinetics were derived. Soda lime was used initially as the absorbent for CO_2 evolution studies in the shaker flask and in respirometric reactors. Subsequently soda-lime was replaced by KOH as the absorbent in the CO_2 evolution measurement studies, because of the observed slower rate of release of CO_2 from soda-lime during the analysis of CO_2. Four methods were used for CO_2 measurement in the shaker flask soil slurry systems and in respirometric reactors: (1) use KOH to trap CO_2 released from soda lime, and then titrate KOH using standard HCl before and after CO_2 absorption; (2) use $Ba(OH)_2$ to trap CO_2 released from soda lime, and then titrate $Ba(OH)_2$ using standard HCl before and after CO_2 absorption; (3) use KOH to trap CO_2 released from soda lime, precipitate the $KHCO_3$ and K_2CO_3 formed, using $BaCl_2$ to get $BaCO_3$ which is filtered, dried and weighed; (4) use KOH to trap CO_2, measure pH of KOH solution before and after CO_2 absorption, calculate CO_2 generated according to the changes of pH values using the developed computer program. The pH method was shown to be most accurate and provided the most reproducible data. Shaker flask slurry systems data on CO_2 production were generated for the same alkyl phenols used in the respirometric soil slurry reactor studies.

Studies on Adsorption/Desorption Equilibria and Kinetics: Soil adsorption kinetics and equilibria are measured using batch well-stirred bottles. The soil was initially air dried and then sieved to pass a 2.00 mm sieve. A 10 g of soil sample was placed in each bottle and mixed with 100 mL of distilled deionized water containing various concentrations of the compound and mercuric chloride to minimize biodegradation. The soil solution ratio was expressed as the oven-dry equivalent mass of adsorbent in grams per volume of solution. The liquid was sampled after 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, and 36 hours. Before the liquid sample was taken, after the predefined time has elapsed, the bottle contents were centrifuged and the liquid sample was withdrawn using a syringe connected to a 0.45 m porous silver membrane filter. The concentration of the chemical compound in the liquid sample was analyzed using three methods: (1) standard extraction (EPA method 604 and 610) with methylene chloride followed by GC/MS analysis; (2) HPLC analysis; and (3) scintillation counting of the ^{14}C using radiolabelled compound. All three analytical methods were calibrated using standard solutions of each compound with concentrations levels of 1, 5, 10, 50, 100 and 150 mg/L. The calibration data is used to convert the peak areas (GC/MS or HPLC) or counts of disintegrations per minute (DPM) for radiolabelled compounds to the actual liquid concentration. In the case of polycyclic aromatic hydrocarbons (PAHs), each chemical was weighed equal to 80% of standard solubility in hexane. Standard solutions containing 60%, 40%, 20% and 10% standard solubility levels were obtained by diluting with hexane. A HPLC column (Supelco LC-PAH 15 cm x 4.6 cm) was used. A plot of peak areas versus the concentration was made to obtain the standard calibration curve for each chemical. For chemicals with extremely low solubility (< 1 ppm), radiolabelled compounds were used with scintillation counting. Standard solutions were made in the same manner and calibrated with counts of disintegrations per minute (DPM). Stock solutions of each PAH chemical were made by first weighing chemical equal to at least twice standard solubility level in water. The chemical was thoroughly mixed with ultrapure water using teflon coated magnetic stir bar for 48 hours. The solution was allowed to settle for 48 hours. The saturated solution was decanted and filtered using a 5 m millipore filter to remove all suspended particles. The liquid concentration was analyzed using either HPLC or scintillation counting. Other stock solutions were obtained by diluting with ultrapure water to obtain solutions with 80%, 60%, 40%, 20% and 10% standard solubility levels.

Desorption studies were conducted by first adsorbing the chemical on to the soil until equilibrium was achieved. Two methods were used for desorption studies. In the first method, 100 ml of deionized distilled water is mixed with 20

grams of soil and specified concentration of chemical for adsorption. After adsorption equilibrium is attained, the whole solution is centrifuged and 90 ml of supernatant is taken out and replaced with an equal volume of deionized distilled water and with 20 gm/l of mercuric chloride to inhibit biodegradation. Desorption begins from this time. A 20 ml sample was withdrawn at 4, 8, 16, 24, 48, 72, 96 and 120 hours from separate bottles. Each sample was filtered with 0.45 m silver membrane filter and extracted with methylene chloride and analyzed using GC/MS technique to determine the concentration of solute. HPLC analysis and ^{14}C scintillation counting analysis for radiolabelled compounds were also used as additional methods for comparative purposes. In the second method, 100 ml of deionized distilled water was mixed with 20 gms of soil and specified concentration of chemical for adsorption. After adsorption equilibrium was attained, the sample was diluted with an equal volume of deionized distilled water, and 20 gm/l of mercuric chloride was added to inhibit biodegradation. A 20 ml sample was withdrawn at 4, 8, 16, 24, 48, 72, 96 and 120 hours from separate adsorption bottles. The sample was analyzed by extraction with methylene chloride followed by GC/MS analysis. HPLC analysis and ^{14}C scintillation counting analysis for radiolabelled compounds were also used as additional methods to compare the analysis results in desorption studies. Results from all three analytical approaches agreed closely, and subsequently HPLC was used exclusively.

Radiochemical Techniques for Determining Biodegradation of Organics in Soil: A radiorespirometric biodegradation protocol was developed for quantitating the biodegradation/mineralization of the organic pollutant compounds in soil slurry systems. The protocol was shown to be particularly applicable to the study of biodegradation of alkyl phenol compounds in the respirometric soil slurry reactors in that it was possible to corroborate the extent of biodegradation data on these compounds as measured by the respirometric oxygen uptake and carbon dioxide evolution in shaker flask systems. Studies were conducted with phenol and each of the alkyl phenols in concentrations of 50, 100 and 150 mg/L in the respirometric reactors. The phenols were added to the OECD nutrient solution made in deionized distilled water and mixed with either 5, 10 or 15% soil. One ml of ^{14}C fully tagged radiolabelled phenol (concentration equals to 1 ci/ml) was added to each of the experimental and control reactors. Five ml of 2N KOH solution is used to absorb the $^{14}CO_2$ released from the solution. After appropriate acclimation time, sampling of KOH in the special holder in the respirometric reactors was initiated by taking out 5 ml KOH volumes with absorbed $^{14}CO_2$ every two hours from each of the reactors. The sampled KOH solution was mixed with a cocktail solution (Ultima Gold) in a 1:10 ratio and analyzed via liquid scintillation counting technology (Packard TRI-CARB 2500 TR Liquid Scintillation Analyzer). Liquid scintillation efficiency tracing technique was used to quantitate the $^{14}CO_2$ concentration released from the solution in the reactor systems.

Determination of Bacterial / Soil Sorption Isotherm: The adsorption isotherm for the bacterial cells was determined by incubating soil microbiota with radiolabelled phenol in a respirometric reactor until an oxygen uptake plateau was obtained, indicating that all phenol has biodegraded either into $^{14}CO_2$, which is adsorbed in the KOH solution and into ^{14}C biomass. The soil suspension was allowed to settle for about 30 minutes. One ml of supernatant is sampled and the ^{14}C activity was measured by liquid scintillation counting. Equilibrium amounts of the ^{14}C biomass adsorbed to the soil was determined by subtracting the ^{14}C present in the biomass in suspension and the ^{14}C present as carbon dioxide absorbed in the KOH solution from the total ^{14}C added initially. The ratio of the biomass adsorbed to the soil and the biomass present in the suspension gives the biomass / soil adsorption isotherm parameter, Kb.

RESULTS AND DISCUSSION

Studies on Soil Microcosm Reactors: With the use of these specially designed microcosm reactors, it was possible to acclimate the indigenous microbiota to mixture of phenol and substituted phenols in one set of reactors and similar performance was obtained for other set of microcosm reactors spiked with a mixture of PAHs. Soil samples from the microcosm reactors are used as a source of acclimated microbiota; for measuring oxygen uptake respirometrically to determine biodegradation kinetics; to determine carbon dioxide generation kinetics; and for radiochemical studies performed respirometrically to quantitate biodegradation data. Cumulative carbon dioxide generation as a function of time for the microcosm reactors, before and after spiking the microcosms (experimental) with solutions comprised of phenolic compounds and PAHs and the control microcosm with OECD nutrients only,

provided evidence of mineralization of respective constituents of the mixtures. The cumulative carbon dioxide production increased after spiking with nutrients and the phenolic and PAH solutions. The GC/MS and HPLC soil data on the residual parent compounds and intermediate metabolites and end products corroborated the CO_2 evolution data and demonstrated conclusive evidence of mineralization of the respective phenolic compounds and the PAH compounds.

Analysis of Oxygen Uptake Data: Respirometric oxygen uptake data were generated for several alkyl phenols using soil slurry systems. The oxygen uptake data for 5% soil concentration with 0, 50, 100, and 150 mg/L of phenol concentrations, indicate that at 0% phenol concentration, the oxygen uptake is due to degradation of soil organic matter, and that the oxygen uptake increases with phenol concentration. The oxygen uptake curves did not change appreciably when the soil concentration was increased, except that the lag time decreased for all phenol and alkyl phenol concentrations. The same trends were demonstrated for substituted phenolic compounds. The oxygen uptake data were analyzed using the mathematical model and the random search technique and the best-fit Monod parameters were generated for the phenolic compounds studied. Except for K_s, the other biokinetic parameters do not vary significantly with changes in phenol or soil concentration. The experimental value of the biomass adsorption parameter, K_b, was 167.0 (mg/Kg)(L/mg). A high value of K_b indicates that a significant amount of active biomass remains attached to the soil particles as compared to the biomass existing as suspended culture.

Oxygen uptake data was generated with 5% soil slurry and the polycyclic aromatic hydrocarbons. 100 mg/L concentration of each PAH was used in the experiments. Initially the PAH compound was insoluble in the nutrient mixture and remained suspended as the mixture was mixed with the soil. However, after some acclimation time, the PAH compound was emulsified in the aqueous mixture. The oxygen uptake data were analyzed using the mathematical model and the best-fit Monod parameters for the PAHs were generated. The Monod kinetic parameter, $_w$, represents aqueous degradation of the dissolved or emulsified compound by the microorganisms present in the aqueous phase. The maximum specific growth rate parameter, $_w$, ranges from 0.127 to 0.482 for the four PAH compounds, which is typical for aerobic aqueous biodegradation of most organic compounds. The yield coefficient, y, is approximately 0.5 which is also typical for aerobic biodegradation. The Monod kinetic parameter, $_{sw}$, for the microorganisms immobilized in the soil matrix, was significantly higher than that for the aqueous phase. The approximate first-order kinetic parameter for the immobilized biomass ($_{sw}/K_{sw}$) is lowest for phenanthrene and highest for naphthalene. This agrees with literature values and with the fact that phenanthrene with three fused aromatic rings is more difficult to biodegrade than naphthalene with two fused aromatic rings.

Measurement of CO_2 Generation Rate: Comparisons were made between the cumulative CO_2 concentrations experimentally measured for the different soil and compound concentrations in the shaker flask soil slurry systems and respirometric reactor soil slurry systems measuring oxygen uptake data. Ratio values were developed for the CO_2 experimentally measured in respirometer and shaker flask to the CO_2 calculated from oxygen uptake data. The compatibility between the data on the CO_2 production in the shaker flask and respirometric vessel tests has been established and verified and the measurement of CO_2 evolution in shaker flask soil slurry systems was shown to be dependable for quantitative CO_2 analysis. The results on the relationship of the two reactor systems provided data on the correlation between the oxygen requirements and CO_2 generation for metabolic activity of microbiota on toxic organics in the soil slurry systems. The total amount of carbon dioxide generated agrees closely with the appropriate amount of oxygen uptake required to mineralize the compound. This demonstrates that complete mineralization of the compound was achieved in the respirometric experiments.

Measurement of $^{14}CO_2$ Generation Rate by Radiorespirometry: Data have been generated on radiolabelled degradation of phenolic and PAH compounds in soil slurry systems spiked with unlabelled compounds for 5 and 10% soil concentration levels. The DPM data indicate that phenols and PAHs are preferred over the organic matter normally present in soil, once the indigenous microbiota are acclimated to these compounds. In the case of phenolic compounds, the data demonstrate that measurement of a carbon dioxide evolution can be used for determining the kinetics of biodegradation for phenol and alkyl phenols in soil slurry systems. Furthermore, analysis of the liquid.

phase showed that little carbon residual remained in the liquid at the end of the experiment suggesting complete mineralization of phenol.

Analysis of Adsorption/Desorption Data: The liquid concentrations for all phenolic compounds and PAHs did not vary more than 5% after 48 hrs, which indicated that equilibrium was achieved. In addition, it can be concluded that since the concentration of the compound did not change after 48 hours even though the experiments were conducted for 96 hours, there was no biological degradation of the compounds under the experimental conditions. The adsorption isotherm for each compound was analyzed using the Freundlich isotherm equation:

$$X/M = k_a C^{1/na} \tag{7}$$

The desorption isotherm for each compound was also analyzed using the Freundlich equation:

$$X/M = k_d C^{1/nd} \tag{8}$$

where (X/M) is the equilibrium concentration in the soil phase, C is the equilibrium concentration in the liquid phase, k_a, k_d are the Freundlich isotherm parameters for adsorption and desorption, respectively, and (1/na), (1/nd) are the adsorption intensity factors for adsorption and desorption respectively. The adsorption kinetics was analyzed using the following equation:

$$dS_w/dt = k_{1a} S_w^{m_a} - k_{-1a} S_s \tag{9}$$

where S_w is the compound concentration in the liquid phase, S_s is the compound concentration in the soil phase and is equal to (X/M) at any time, t, and k_{1a}, k_{-1a} and m_a are the kinetic parameters for adsorption.

The desorption kinetics was analyzed using an equation similar to that for adsorption kinetics:

$$dS_w/dt = k_{1d} S_w^{m_d} - k_{-1d} S_s \tag{10}$$

where k_{1d}, k_{-1d} and m_d are the kinetic parameters for desorption.

Data were generated on the Freundlich isotherm adsorption and desorption parameters, adsorption intensity coefficients and adsorption and desorption kinetic parameters for phenol, 2,4 dimethyl phenol, p-cresol, catechol, hydroquinone and resorcinol. The adsorption isotherms were nonlinear and the desorption isotherm linear for the phenolic compounds studied. Therefore, a combination of nonlinear adsorption and linear desorption equations were used in the analysis. Data were generated on the adsorption/desorption kinetic and equilibrium isotherm parameters for the PAH compounds studied. In the case of phenols , the adsorption kinetics exhibited an initial fast partitioning of the compound in the soil organic matter followed by a significantly slower adsorption on the soil mineral matter. The adsorption isotherms were nonlinear and were fitted using the Freundlich isotherm equation. The desorption kinetics was significantly slower than the adsorption rate and a linear isotherm was found to adequately fit the equilibrium data. In the case of the representative kinetic data for the PAHs, naphthalene and phenanthrene, for all the concentrations tested , equilibrium is attained in about 20 hours. For naphthalene, approximately 45% of the initial amount of compound is adsorbed by the time equilibrium is attained, and this percent adsorption does not vary significantly with initial concentration. However, in the case of phenanthrene, about 85% of the initial amount of compound is adsorbed until equilibrium is attained. This increase in relative percent adsorption is mainly due to partitioning into the soil organic matter which depends on the compound's octanol-water partition coefficient. The octanol partition coefficient for phenanthrene is about 60% higher than that for naphthalene. Desorption is usually slower than adsorption and equilibrium for all concentration tested is attained in about 50 hours. The adsorption/desorption equilibria and kinetics data demonstrate that in soil slurry bioreactors, if the soil microbiota is acclimated to the phenolic and PAH compounds, the aqueous biodegradation rate is inherently controlled by the desorption rates of the compounds from the soil matrix.

CONCLUSIONS

Respirometric studies with soil slurry reactors provides valuable insight into the biodegradation kinetics of compounds in the presence of soil. It has been shown that a Monod kinetic equation in conjunction with a linear adsorption isotherm can provide reliable estimates of the Monod kinetic parameters and the adsorption coefficient. Carbon dioxide generation in soil slurry systems provides unambiguous measurements of the rate of mineralization of the compound in the presence of soil. A protocol developed for quantitative measurement of $^{14}CO_2$ evolution rate by radiorespirometry provides confirmation of mineralization kinetics from carbon dioxide evolution studies and ensures that the net CO_2 is generated from mineralization of the compound and not due to natural soil respiration.

Further studies are planned for measuring the biokinetics of compounds in compacted soil systems, as opposed to our current measurements in soil slurry systems. This will allow one to determine the impact of soil compaction, oxygen transfer rates, and moisture content on biodegradation. A attempt will also be made to develop a detailed mathematical model implemented as a computer program, that will use our experimental data and model parameters to actually quantify rates of bioremediation at contaminated sites.

REFERENCES

1. Tabak, H.H. and R. Govind. "Determining Biodegradation Kinetics with use of Respirometry for Development of Predictive Structure-Biodegradation Relationship Models." Presented at the 4th International IGT Symposium, 1991 Colarado Springs, CO. Published in Gas, Oil and Environmental Biotechnology. Volume 4. C. Akin, R. Markuszeski, J. Smith (eds.) 1992. p.129

2. Tabak, H.H., L. Lai, X. Yan, C. Gao, S. Kim, S. Pfanstiel and R. Govind. "Methodology for Testing Biodegradability and Determining Bioavailability and Biodegradation Kinetics of Toxic Organics in Soil." Presented at the 5th International IGT Symposium on Gas, Oil and Environmental Biotechnology, Chicago, IL, Sept. 21-23, 1992. To be published in Gas , Oil, Coal and Environmental Biotechnology V, Institute of Gas Technology, Chicago, IL., 1993.

3. Tabak, H.H., C. Gao, L. Lai, X. Yan, S. Pfanstiel, S. Kim, and R. Govind. "Determination of Biodegradability and Biodegradation Kinetics of Phenol and Alkyl Phenols". Presented at the 1992 ACS Industrial and Engineering Chemistry Division Symposium on "Emerging Technologies for Hazardous Waste Management". Special Symposium on Bioremediation of Soils and Sediments. Atlanta, Georgia, September 21-23, 1992. Published in 1993 Emerging Technologies in Hazardous Waste Management, ACS Symposium Series, Volume IV, 1993.

4. Tabak, H.H., R. Govind, C. Gao, L. Lai, X. Yan, S. Kim, 1992. "Determination of Biodegradability and Biodegradation Kinetics of Organic Compounds in Soils". Presented at the 1992 ACS Industrial and Engineering Chemistry Division Symposium on "Emerging Technologies for Hazardous Waste Management". Special Symposium on Bioremediation of Soils and Sediments. Atlanta, Georgia, September 21-23, 1992. Published in 1993 Emerging Technologies in Hazardous Waste Management, ACS Symposium Series, Volume IV, 1993.

5. Govind, R., C. Gao, L. Lai, X. Yan, S. Pfanstiel, I. S. Kim and Tabak, H.H.1993. " Development of Methodology for the Determination of Biodegradability and Biodegradation Kinetics of Toxic Organic Pollutant Compounds in Soils". Paper presented at the In-Situ and On-Site Bioreclamation, 2nd International Symposium, San Diego, CA, April 5-8, 1993. Published in the 1993 On-site Bioreclamation Processes for Xenobiotic and Hydrocarbon Treatment, Battelle Memorial Institute, Columbus, Ohio.

6. Tabak, H.H., C. Gao, X. Yan, L. Lai, S. Pfanstiel, C. Fu and R. Govind. "Kinetics of Biodegradation, Adsorption and Desorption of Alkyl Phenols and Polycyclic Aromatic Hydrocarbons in Soil Slurry Systems" Presented at the 6th International IGT Symposium on Gas, Oil and Environmental Biotechnology. The Broadmoor Hotel, Colorado Springs, CO, November 29-December 1, 1993. To be published in Gas , Oil, Coal and Environmental Biotechnology VI, Institute of Gas Technology, Chicago, IL., 1994

MEMBRANE BIOFILTRATION IN ANAEROBIC/AEROBIC APPLICATIONS

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INTRODUCTION

The 1989 SARA emission summary for petroleum and chemical manufacturing companies shows that the largest releases are of volatile organic compounds (VOCs) in air. Current technologies for treating VOCs are limited and include activated carbon adsorption, wet scrubbing and incineration. An emerging technology for treatment of VOCs involves the use of biofilters.

Currently, most biofilter studies have involved packed beds of soil, peat or compost, pelletized packed beds or straight passages ceramic monoliths[1,2,3]. In all these studies, the contaminated air stream is contacted with a biofilm immobilized on a support material. Due to the presence of oxygen in the contaminated air stream and high oxygen transfer rates, aerobic degradation of the contaminants occurs in the biofilms. However, certain organics, like trichloroethylene or parachloroethylene, either require a cometabolite under aerobic degradation conditions or biotransform only under anaerobic conditions. The challenge in biofiltration of such compounds is to create anoxic/anaerobic conditions when the contaminants are present in an air stream.

In this study, a hollow fiber porous membrane module was used as a biofilter. Biomass is immobilized on the outside of the hollow fibers and the shell side is filled with nutrient mixture, which flows at a low flowrate. The contaminated gas stream, containing toluene is passed through the hollow fibers. The contaminant, in this case, toluene, dissolves in the liquid in the membrane pores, diffuses into the biofilm on the shell side and biodegrades. Since oxygen transfer is now limited by the dissolution and diffusion steps, anoxic or anaerobic conditions can be created on the shell side biofilm. This enables the biotransformation of compounds that are otherwise recalcitrant under aerobic conditions. Figure 1 schematically shows the mechanism of pollutant dissolution, diffusion in the liquid phase and ultimate biotransformation in the biofilm. The shaded zones shows the oxygen transfer into the biofilm. As the biofilm grows on the shell side, the biofilm outside the shaded zone becomes anoxic/anaerobic due to oxygen consumption in the aerobic zone. The pollutant degrades in the anoxic zone and the biotranformation products degrade in the aerobic biofilm as they diffuse back into the hollowfiber side.

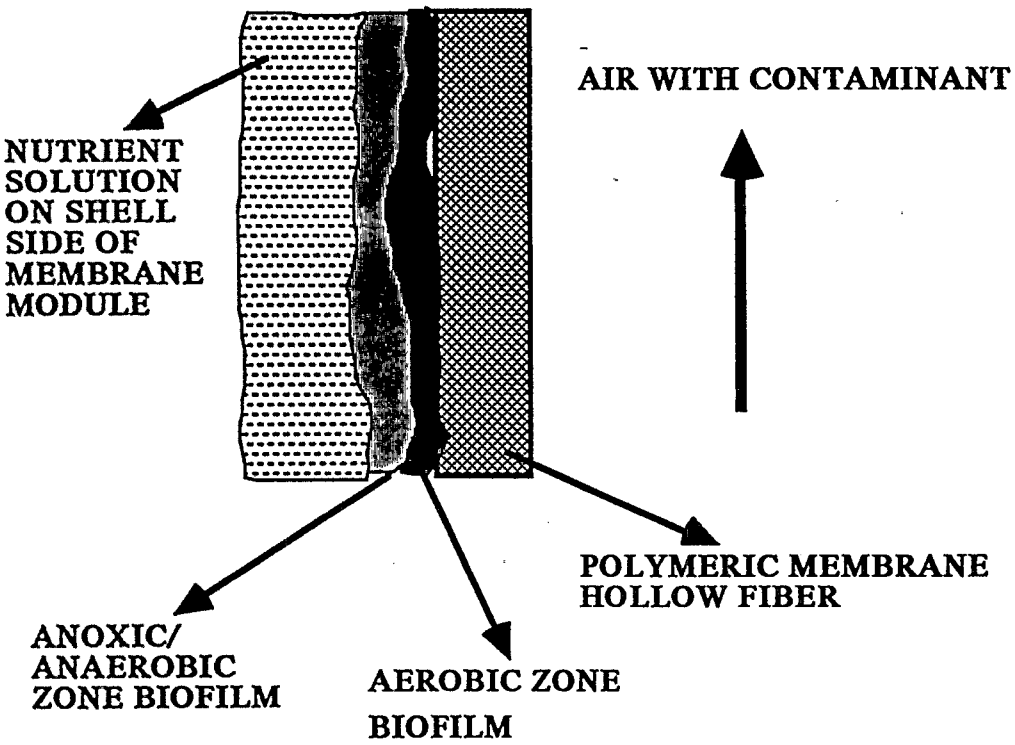


Figure 1. Schematic showing the aerobic and anoxic zones in a hollow fiber membrane biofilter. The contaminant biotransforms in the anoxic zone and the degradation products mineralize in the aerobic zone.

EXPERIMENTAL STUDIES

Figure 2 shows a schematic of the experimental apparatus. Two hollow fiber modules were connected in series and toluene contaminated air was passed through the hollow fibers. Nutrient mixture was recirculated through the shell side of each membrane module. Table 1 summarizes the design and operating conditions of the experimental system.

RESULTS AND DISCUSSION

Preliminary studies were conducted with an inlet toluene concentration of 200 ppmv. As shown in Figure 3, the biofilter removal efficiency increased steadily due to biofilm development on the shell side of the hollow fibers. When the removal efficiency had increased to about 70%, the inlet toluene concentration was increased to 400 ppmv. After an initial decrease in removal efficiency, the removal efficiency increased attaining about 72%. Further increases in inlet toluene concentration resulted in a similar response with an initial decrease in removal efficiency followed by a gradual increase to its initial value.

Further experiments are planned with contaminants such as trichloroethylene (TCE) and parachloroethylene (PCE).

REFERENCES

1. Utgikar, V., R. Govind, Y.G. Shan, R.C. Brenner, and S.I. Safferman, "Biodegradation of Volatile Organic Compounds in a Biofilter," In "Emerging Technologies for Hazardous Waste Management II," Tedder, D.W., and F.G. Pohland, Eds., ACS Symposium Series 468, ACS, Washington, DC (1991).

2. Govind, R. and D. F. Bishop, "Environmental Bioremediation Using Biofilters", Presented at Frontiers in Bioprocessing III, Boulder, CO, September 19-23, 1993. Paper to be published in Conference Proceedings.

3. Govind, R. and Dolloff F. Bishop, "Advances in Gas Phase Biofiltration Applications for Volatile Organic Compounds (VOC) Control", Paper presented at the HazMat 93 North-Am Conference, October 12-14, 1993, Detroit, MI. Paper published in Conference Proceedings.

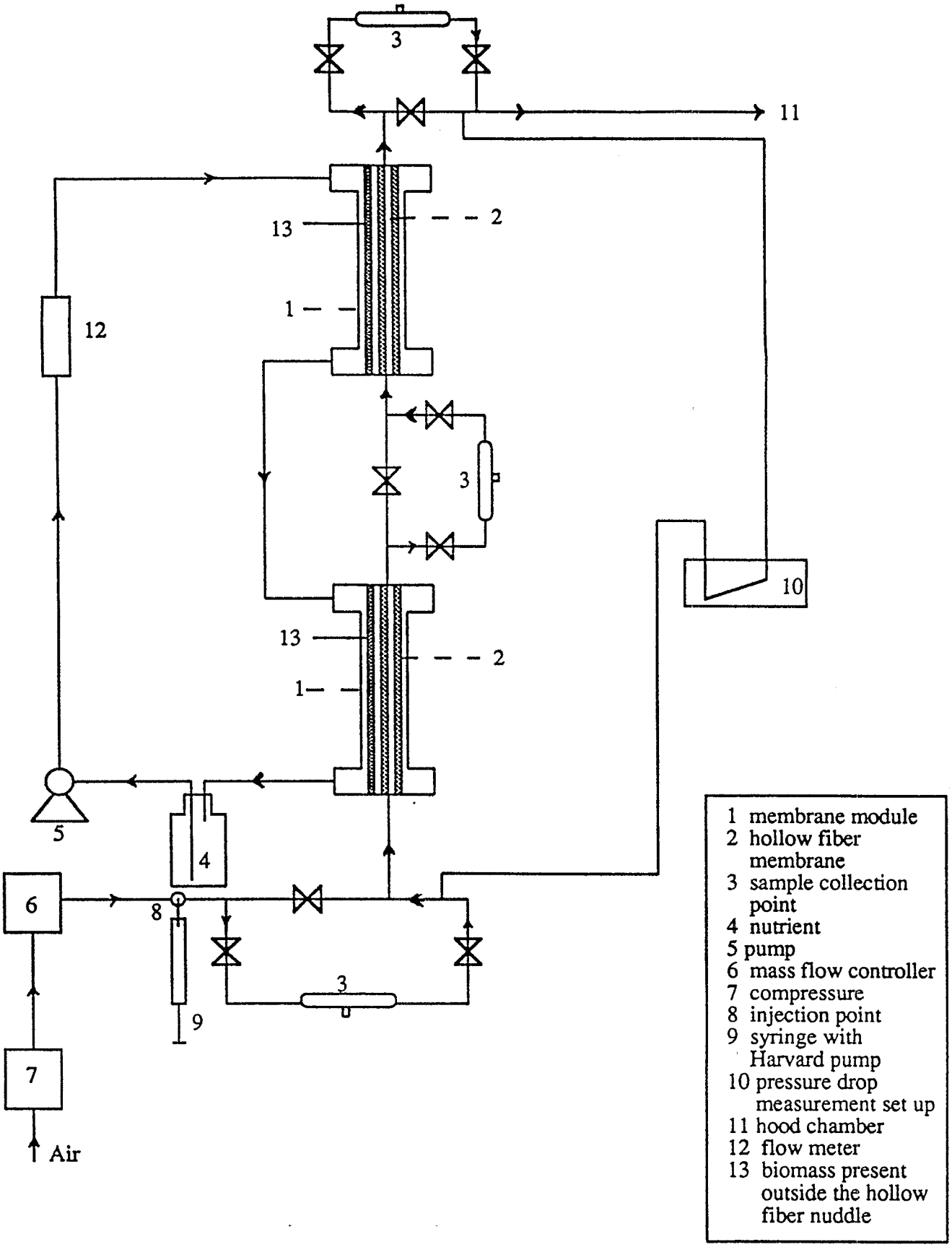
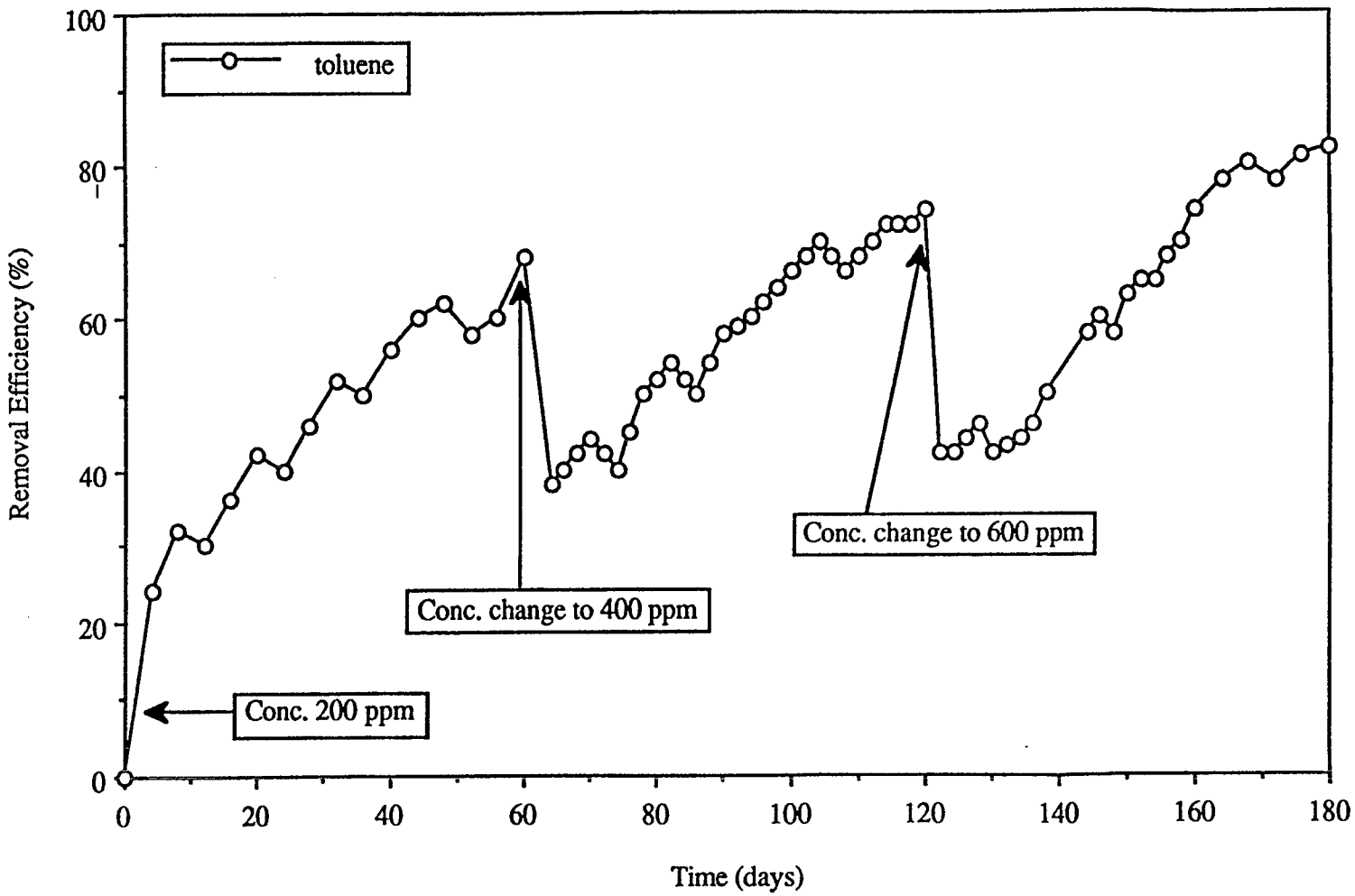


Figure 2. Schematic of the membrane biofilter experimental apparatus.

Table 1. Summary of the design and operating conditions for the membrane biofilter system.

Air flow rate	80 ml/min
Amicon Hollow Fiber Cartridge (Model NO : H1P10-43)	
Number of hollow fiber nuddles present per Cartridge	51
Length of each hollow fiber nuddle	12.5 cm
Internal diameter of each fiber	0.11 cm
Outside diameter of each fiber	0.19 cm
Active membrane surface area per Cartridge	278.7 sq cm
Total internal volume of hollow fiber nuddles (for 2 cartridge)	21.26 ml
Residence time	15 seconds (approx)
Toluene concentration	600 ppm
Nutrient flow rate	10 ml/min
pH of nutrient solution	7.24
temp	25 oC
Removal efficiency (at present)	80 (%)

Figure 3. Removal Efficiency of the membrane biofilter system for treating toluene in air.



RECENT ADVANCES IN BIOFILTRATION

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INTRODUCTION

Biofiltration involves contacting a contaminated gas stream with microorganisms in a contactor and is emerging as an attractive technology for the removal of low concentrations (< 600 ppmv) of volatile organic chemicals (VOCs) from air. Compared to other technologies, biofiltration is inexpensive, reliable and requires no post-treatment. It can be applied to any biodegradable VOC emission problem - from manufacturing and processing units, wastewater and landfill leachate treatment plants (Utgikar et al, 1991)[1], and soil remediation operations, such as vacuum extraction.

Recently, studies have been conducted on the use of pelletized and ceramic structured media in biofiltration (Utgikar et al., 1991; Govind et al., 1993a, 1993b)[1,2,3]. Conventional applications of biofilters use fine or irregular support media, such as soil, peat or compost. Biofilters with pellets or structured media potentially have significant advantages over conventional biofilters, including better gas distribution, improved pH control by using buffers in the liquid medium trickling through the bed, and the capability for removal of excess biomass from the media.

These improved biofilters have been used at bench and pilot scale to treat VOCs air stripped from landfill leachate streams using adsorbent and non-adsorbent media. Nearly complete removal of almost all of the aerobically degradable compounds were achieved in these biofilters. Intrinsic microbial degradation kinetics in immobilized biofilms were determined using novel experimental systems. Mathematical models were developed to describe VOC biodegradation in these biofilters.

Ongoing research and development on improved biofiltration include evaluation of the operational dynamics, media cleaning and scale-up requirements and use of alternate media capable of sustaining different kinds of microorganisms.

LIMITATIONS OF CURRENT SYSTEMS

Soil biofilters are relatively large compared to filters using other media, primarily due to the fact that soil pores are smaller and compounds have much lower permeability in soil (Bohn, 1992)[4]. Soil biofilters also have limited depths due to problems associated with maintaining humidity in soil and minimizing pressure drop. Furthermore, soil sorption capacity is limited and residual contaminant is vented immediately to the atmosphere (Bohn and Bohn, 1988)[5].

Peat/compost biofilters are suitable for treating large volumes of air containing easily biodegradable VOCs at low concentrations. However, both soil and peat/compost biofilters are susceptible to channeling and maldistribution of the air stream. This leads to uneven biogrowth as well as drying of the bed. Both of these effects adversely impact biofilter performance. Soil and peat/compost biofilters require humidification, and nutrients cannot be supplied continuously. End products of biomass decay cannot be washed out of the filters and ultimately require media replacement. When VOCs contain organic chlorine, sulfur or nitrogen, the support media has to neutralize degradation products which are acidic.

Developmental needs for improving biofiltration include: (1) improved control of moisture and nutrients in the biofilter bed; (2) improved control of acids (pH) and other inhibitory degradation products; (3) methods for control of excess biomass to prevent clogging and media replacement; and (4) improved approaches and media that use adapted or engineered organisms and novel reactor configurations for degradation of recalcitrant VOCs.

CURRENT DEVELOPMENTS

To meet these needs, extensive work has been conducted by EPA's Risk Reduction Engineering Laboratory and the University of Cincinnati on biofilters with novel media and operational approaches (Govind et al., 1993a, 1993b, 1993c)[2,3,6]. The research featured studies to: (a) demonstrate system feasibility for degrading representative VOCs; (b) evaluate intrinsic kinetics of VOC degradation; and (c) develop mathematical models for improved biofilters.

Representative VOCs included compounds with a range of aqueous solubilities and octanol-water partition coefficients. These compounds were iso-pentane, toluene, methylene chloride, trichloroethylene (TCE), ethylbenzene and chlorobenzene. Support media used in these studies included activated carbon pellets, ceramic celite pellets and corrugated plates (Manville Corporation, Denver, CO), and extruded ceramic monoliths with high surface area to volume ratio (Corning Glass, Inc., Corning, NY). Comparative studies were conducted with peat/compost biofilters. Control studies were also conducted to investigate adsorption/desorption of contaminants on the media in the absence of bioactivity.

RESULTS AND DISCUSSION

Biofilter performances were expressed in terms of removal efficiencies of the compounds. Removal efficiency of the biofilter for each compound was calculated from the amount of compound removed per unit time in the biofilter, expressed as a percentage of the amount of that compound entering the biofilter per unit time. Design and operating conditions for each biofilter are summarized in Table 1.

Packed bed peat and compost biofilters

Abiotic control tests with both peat and compost materials showed poor adsorption of iso-pentane. For both materials, the exit gas composition of isopentane became equal to the inlet concentration (350 ppm) in about 30 minutes. For both materials, the removal efficiency increases with decreasing inlet gas concentration and increasing gas residence time. The compost material showed higher removal efficiencies for isopentane at 360 ppmv inlet concentration than the peat material. At higher inlet concentrations, the two materials showed similar results.

The effect of water content in the peat and compost material was studied experimentally. Experiments were conducted with both increasing and decreasing water content in the peat/compost material. For peat, when the water content decreased below a critical value of 0.48 gms water/gms of dry peat, the biofilter did not recover its removal efficiency when the water content of the material was increased. For compost, a similar effect was observed below water content of 0.58 gms water/gms of dry compost.

Table 1. Design and Operating Conditions for the Biofilter Studies

	DESIGN				OPERATING		
Media Type	Diameter (cm)	Height (cm)	Volume (cm^3)	Influent COD (gm/L.day)	NH_3-N (ppm)	Nutrient Loading (L/m^2.day)	Compounds (conc. in ppm)
Peat	5.0	70	1374	0.1 - 1.9	-	-	Iso-pentane (360 - 960)
Compost	5.0	70	1374	0.1 - 1.9	-	-	Iso-pentane (360 - 960)
Activated carbon pellets (3 mm)	2.5	60	294	1.6	7	1,000	Toluene (520), Methylene Chloride (180), Trichloroethylene (25)
Ceramic Celite pellets (6 mm)	2.5	90	1767	1.3	7	250	Toluene (450), Methylene Chloride (150), TCE (25), Chlorobenzene (40), Ethylbenzene (25)
Celite Straight passages (99 square passages of 6 mm size)	10 x 10	90	9,000	0.77 - 2.1	7 - 12	150	Toluene (450), Methylene Chloride (150), TCE (25), Chlorobenzene (40), Ethylbenzene (25)

This irreversible damage to the peat/compost material was caused by substantial irreversible shrinkage of the peat/compost material below the critical water content, resulting in cracks and voids in the bed through which the gas could easily bypass the bed. Addition of water to the material did not cause the material to expand and fill the cracks and voids caused by the shrinkage. This showed that maintaining water content through proper humidification of peat/compost materials was essential for continued efficient biofilter operation.

The isopentane removal efficiency increased with increasing water content until an optimal value was attained (0.56 for peat and 0.65 for compost). When the water content was increased above this optimal value, the removal efficiency decreased for both materials. This decrease in removal efficiency probably resulted from the partial filling of bed void fraction with free water causing mass transfer limitations for the degradation of isopentane. This again emphasizes the importance of maintaining water content in peat/compost materials at or near the optimal value.

Removal efficiencies increased with temperature for both materials. Both materials showed maximum removal efficiencies above bed temperature of 35°C. Below 25°C, the removal efficiency decreased almost linearly with temperature. If the bed temperature is below 20°C, substantial improvements in performance could be achieved by heating the inlet air to increase the bed temperature.

Activated carbon biofilter

Removal efficiency of the biofilter was studied as a function of time for toluene, methylene chloride and trichloroethylene (TCE) at an inlet gas flow rate of 150 ml/min. This flow rate produced a gas retention time of 2 minutes in the biofilter bed. Initially the biofilter exhibited high removal efficiency for all three compounds due to adsorption of the compounds on the activated carbon. However, as the carbon became saturated, the removal efficiencies decreased until the microorganisms started to grow. The removal efficiencies increased, attaining nearly 100% in about 80 days after the initial start up of the system. The carbon biofilter, as the first system studied, did not have optimum startup since insufficient ammonia in the nutrients limited biomass growth. Subsequent increase in nutrient ammonia accelerated biofilm development after about 40 days, producing 100% removal efficiencies for all three compounds.

The activated carbon biofilter after acclimation effectively treated (> 99% removals) toluene, methylene chloride and trichloroethylene for about 4 months without loss of treatment efficiency. After 4 months of operation, the gas flow rate was reduced to 50 ml/min. since the biofilter was beginning to flood at higher flow rate. Flooding resulted from plugging of the biofilter bed due to excessive biomass growth. Biomass growth and plugging of the biofilter was reflected in greater pressure drop across the bed.

Ceramic Celite packed bed Biofilter

The removal efficiency of the ceramic celite packed bed biofilter was studied for five compounds (toluene, methylene chloride, TCE, ethylbenzene, chlorobenzene) as a function of time. Removal efficiencies gradually increased to nearly 100% for all the compounds except trichloroethylene (TCE). This rise indicated that biomass growth occurred during this period, ultimately building enough biomass to degrade the compounds completely.

The celite biofilter was as successful in removing the compounds, except for trichloroethylene, as the activated carbon biofilter. Folsom et al. (1990)[7] have shown that trichloroethylene is degraded only as a secondary substrate in the presence of a primary metabolite, such as toluene or phenol. The biodegradation rate of toluene is much faster than that of TCE. As toluene entered the bottom of the biofilter, it was rapidly removed in the bottom third of the biofilter. The removal was confirmed by determining the concentration profile of the compounds in the celite biofilter through analyzing samples withdrawn from side ports located along the height of the biofilter. As a result, toluene was not available as a primary metabolite to trigger TCE degradation in the rest of the biofilter.

With the activated carbon biofilter, toluene fed through the gas phase was also consumed rapidly. However, toluene adsorbed on the activated carbon during the initial period provided primary carbon source for TCE degradation in the rest of the column. A toluene reservoir is not possible in case of celite, which is essentially a non-adsorbent support medium.

After 6 months of operation, the celite packed bed biofilter plugged due to biomass growth. Studies were conducted on cleaning the pellets using water at room temperature. At biomass loadings above 5 weight percent of the clean celite pellets, biomass loss was high initially. At low biomass loadings, loss of biomass from the pellets was small. Further, the amount of water required to clean the pellets was significant. High (> 5) water to pellet weight ratios may be a problem since significant amounts of wastewater would be generated and adequete water handling systems would be required.

Ceramic Celite Plates Straight Passages Biofilter

The removal efficiency of the biofilter was studied as a function of time for all the five compounds. The removal efficiency curves indicate that near complete removals of all the compounds except TCE were obtained at the flow rate of 600 ml/min. Gas chromatographic analysis of the exit air stream did not detect any degradation products. As in earlier studies, the carbon dioxide increase in gas streams and the chloride ion increase in the nutrient stream were monitored. The results indicated that removed compounds had undergone full biological mineralization.

Biomass loss in the nutrient solution was characterized by collecting samples of the nutrient solutions and drying them at 100 ^{o}C. The effect of nutrient flow rate on biomass loss rate from the biofilter was measured. The biomass loss from the biofilter is affected by nutrient flow rate and the total biomass loading in the biofilter, which depends on the gas flow rate and its inlet composition.

To increase TCE removal efficiency and demonstrate that lower TCE removal efficiencies were due to lack of toluene, another co-metabolite, phenol, was added to the nutrient media at a concentration of 5 mg/L. Increased TCE removal efficiency was observed after phenol addition to the nutrient media. Complete removal of TCE was achieved when inlet TCE concentration was reduced from 25 ppm to 10 ppm.

Degradation rates achieved in the experimental straight passages biofilter were mainly limited by the low surface area of the celite plates. With recent developments in extruded ceramic monoliths, significantly higher surface area per unit volume can be obtained commercially. Using such high surface area extruded monoliths, significantly higher biomas loadings and hence higher degradation rates per unit biofilter volume can be realized.

CONCLUSIONS

Biofilters using porous pellet or structured (straight-passages) media and recycled nutrient and buffer solutions have potential advantages over conventional soil or peat/compost biofilters for removal of biodegradable VOCs from contaminated air. These include:

- improved distribution of air flow and moisture control in the media, increasing process performance;
- improved neutralization of mineral acid degradation products (pH control);
- increased capacity for treating higher VOC loadings (300 -600 ppmv); and
- capability for removal of excess biomass from the biofilter, thus preventing clogging and eventual media replacement.

Biofilters with porous pellet media, however, require development of effective cleaning methods for field-scale applications. Biofilters with structured media (straight passages) offer easier cleaning options, including release of biomass (self cleaning) into the recycling nutrient and buffer solution.

Basic research areas currently being investigated to exploit the full potential of structured media (straight passages) biofilters include the following:

- quantification of biomass release, which depends on the shear force exerted on the biofilm by trickling nutrients, amount of biomass present in the biofilter and substrate load;
- quantification of biofilm adhesion to the media surface, which controls the release of the biomass. Biomass attachment also impacts biofilter removal efficiency during startup and transient operation.

Other research needs in biofiltration include:

- evaluation of biofilter dynamic responses to variable flowrates and contaminant concentration;
- proper design guidelines for selection of operational parameters in industrial biofilters. These guidelines would enable proper selection of media and media dimensions, flowrate and composition of nutrient solution, countercurrent or cocurrent mode of operation, methods for initial seeding of biomass, biofilter media cleaning methods and frequency of cleaning.

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LITERATURE CITED

1. Utgikar, V., R. Govind, Y.G. Shan, R.C. Brenner, and S.I. Safferman, "Biodegradation of Volatile Organic Compounds in a Biofilter," In "Emerging Technologies for Hazardous Waste Management II," Tedder, D.W., and F.G. Pohland, Eds., ACS Symposium Series 468, ACS, Washington, DC (1991).

2. Govind, R. and D. F. Bishop, "Environmental Bioremediation Using Biofilters", Presented at Frontiers in Bioprocessing III, Boulder, CO, September 19-23, 1993. Paper to be published in Conference Proceedings.

3. Govind, R. and Dolloff F. Bishop, "Advances in Gas Phase Biofiltration Applications for Volatile Organic Compounds (VOC) Control", Paper presented at the HazMat 93 North-Am Conference, October 12-14, 1993, Detroit, MI. Paper published in Conference Proceedings.

4. Bohn, H.L., "Consider Biofiltration for Decontaminating Gases," Chem. Eng. Progr., **88(4)**, 34 (1992).

5. Bohn, H., and R. Bohn, "Soil Beds Weed out Air Pollutants," Chem. Eng., **95(6)**, 73 (1988).

6. Govind, R. and Dolloff F. Bishop, "Development of Novel Biofilters for Treatment of Volatile Organic Compounds (VOCs)", Paper presented at the IGT Symposium on Gas, Oil and Environmental Biotechnology, Colorado Springs, CO, November 29-December 3, 1993. Paper to be published in Conference Proceedings.

7. Folsom, B.R., P.J. Chapman, and P.H. Pritchard, "Phenol and Trichloroethylene Degradation by Pseudomonas cepacia G4: Kinetics and Interactions Between Substrates," Appl. Environ. Microbiol., **56**, 1279 (1990).

REMEDIATION OF CONTAMINANTS WITH BIOLOGICAL ACTIVATED CARBON SYSTEMS

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INTRODUCTION

The conventional approaches to above-ground treatment of groundwater contaminated with volatile organic compounds (VOCs) involve either liquid-phase adsorption by granular activated carbon (GAC) or air stripping. In these processes, the VOCs are simply transferred from one phase to another without degradation. As a result, further treatment or disposal of the receiving phase is often required. As an alternative, biological treatment has the potential to completely destroy contaminant compounds. Biological processes, however, are frequently perceived as being less stable than physical-chemical approaches, and thus are not always considered for groundwater treatment.

Biological activated carbon (BAC) integrates biological removal and GAC adsorption into a single unit process [1, 2]. In systems designed as adsorbers, it has been shown that biodegradation increases the period between GAC regeneration cycles [3]. In biofilm systems, the use of GAC as a biomass carrier has been shown to remove the compounds resistant to biodegradation and provide enhanced removal during loading transients [4, 5].

In this research, laboratory and pilot-scale fluidized bed systems (BAC-FBR) employing GAC as a biomass carrier were used for the treatment of groundwater contaminated with the gasoline constituents, benzene, toluene and xylene (BTX). The systems were evaluated during start-up, under pseudo-steady-state conditions and following a step increase in influent loading. The Investigation focused on isolating the contributions of adsorption and biodegradation to system performance.

METHODOLOGY

FBRs of three different sizes were used in this work. The dimensions and operational parameters are listed in table 1. The reactors were operated as one-pass systems without recycle (Figure 1). The groundwater was oxygenated to a concentration sufficient to maintain an effluent dissolved oxygen concentration (DO) of more than 4 mg/L and supplemented with nitrogen and phosphorous at a weight ratio of 100:5:1, COD:N:P. The target compounds were injected into feed water using a syringe pump and dissolved using a mixer unit. This contaminated water was then pumped to the bottom of the reactors using peristaltic pumps. The reactors were inoculated with a mixed culture obtained from a pilot-scale FBR that was originally seeded with activated sludge and has subsequently been supplied with BTX as the sole carbon source for more than two years.

This project was divided into three phases. 1) Two 1" laboratory-scale fluidized bed systems were operated in parallel for the comparison of adsorptive and non-adsorptive biofilm carriers. One reactor (FBR) was charged with baker product, a non-adsorptive carbon, and another (BAC-FBR) was charged with GAC. The systems were evaluated in a start-up, pseudo-steady-state and step-load increase conditions. During the step-load increase experiment, the concentration of BTX was increased in 4-fold for 8 hours while keeping the flow constant. 2) A 2" laboratory-scale BAC-FBR charged with GAC was used to treat toluene contaminated groundwater. The amount of adsorbed toluene on BAC particles was measured at regular intervals during start-up, and before and after a 77-hour 4-fold step-load increase. 3) Toluene contaminated groundwater was treated in a 3" pilot-scale BAC-FBR for a period of 1 year. During this operational period, BAC particles were collected from the reactor and subjected to adsorption isotherms for the measurement of adsorption capacity. Isotherms for toluene were performed using a bottle-point method [5].

BTX concentrations were determined using a gas chromatograph equipped with a flame ionization detector (FID), a helium carrier gas, and an automated headspace sampler. The accuracy for measurement

of a sample containing a concentration of 1.5 μg/L was ± 0.1 μg/L. Influent and effluent DO were analyzed using a polarographic electrode coupled to a digital pH/millivolt meter.

TABLE 1. THE DIMENSIONS AND OPERATION PARAMETERS OF FBRS

	1" laboratory-scale FBR	1" laboratory-scale BAC-FBR	2" laboratory-scale BAC-FBR	3" pilot-scale BAC-FBR
Dimensions of FBRs Diameter Height Working Volume	 2.54 cm (1 in) 92/184 cm (3/6 ft)* 0.5/1 liter	 2.54 cm (1 in) 92/184 cm (3/6 ft)* 0.5/1 liter	 5 cm (2 in) 184 cm (6 ft) 4 liter	 7.62 cm (3 in) 322 cm (10 1/2 ft) 14.68 liter
Column Material	glass	glass	glass	PVC†
Carrier Media	Baker Product‡ 20/30 mesh (0.75 mm)	GAC F-400§ 20/30 mesh (0.75 mm)	GAC F-400§ 20/30 mesh (0.75 mm)	GAC F-400§ 18/20 mesh (0.75 mm)
Flow Rate	0.14/0.3 liter/min	0.14/0.3 liter/min	0.9 liter/min	2.2 liter/min
Hydraulic Flux Rate	0.29/0.61 m^3/min-m^2	0.29/0.61 m^3/min-m^2	0.44 m^3/min-m^2	0.48 m^3/min-m^2
Empty Bed Retention Time	3.6/3.3 min	3.6/3.3 min	4.4 min	6.7 min
Target Compounds	BTX	BTX	Toluene	Toluene
Organic Loading Rate	3.4 kg COD/m^3-day 6.0 kg COD/m^3-day	3.4 kg COD/m^3-day 6.0 kg COD/m^3-day	5.3 kg COD/m^3-day	1.4 kg COD/m^3-day
Temperature	15 °C	15 °C	15 °C	20°C

* 1" laboratory-scale fluidized bed systems were set in two configurations. The 0.5 liter setting was used for low organic loading experiment and 1 liter setting was used for high organic loading experiment.
† polyvinyl acetate; ‡ Baker product is the non-adsorptive carbon; § Calgon Fitrasorb 400.

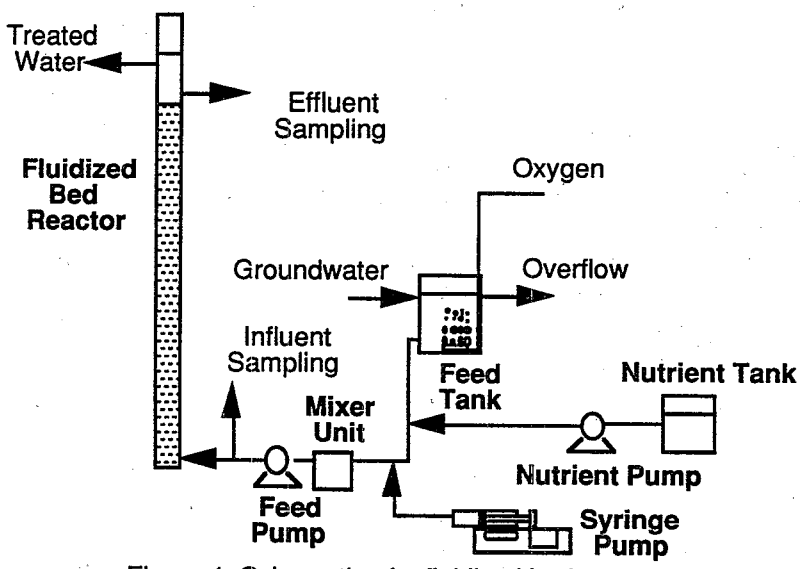

Figure 1. Schematic of a fluidized bed system.

RESULTS

In phase one of this work, two FBRs were operated in parallel. The BAC-FBR utilized both adsorption and biodegradation as removal mechanisms and the FBR operated with biodegradation as the only significant removal mechanism. During the start-up period, the BAC-FBR performed as an adsorption column. Effluent benzene concentration increased up to 50% of influent level at 140 operation hours. After this period, the DO consumption and the carbon bed height started to increase and the

concentration of benzene in the effluent decreased. This indicated the development of significant biological activity and biofilm growth in the BAC-FBR. During the entire start-up period, effluent concentrations of toluene and *p*-xylene were maintained at very low level of 15 μg/L and 18 μg/L, respectively. In the FBR system, breakthrough of BTX occurred soon after introduction of the influent BTX. After approximately 400 operation hours, sufficient biomass had developed on the baker product and the concentrations of BTX in the effluent started to decrease. The DO consumption and bed height also increased. As a result, a large amount of BTX was not treated by the FBR: average removals were only 33%, 40%, and 40% for benzene, toluene and xylene, respectively. In contrast, the BAC-FBR was achieved 91%, 98%, and 98% for benzene, toluene and xylene, respectively, during start-up.

After a mature biofilm developed on the carbon, effluent BTX and DO consumption levels stabilized and the FBRs were assumed to be operating under pseudo-steady-state conditions. In the first test, the average total COD in the influent of the BAC-FBR was 9.6 mg/L (an organic loading rate of 3.8 kg COD/m^3-day) and removals were 99.7%, 99.6%, and 92% for benzene, toluene and xylene, respectively (Table 2.). A 7.3 mg COD/L (an organic loading rate of 2.9 kg COD/m^3-day) was applied on FBR and the removals were 94.6%, 94.7%, and 90.7% for benzene, toluene and xylene, respectively (Table 2.). In the second test, the organic loading rates were increased in both reactors to 6.0 kg COD/m^3-day. The two FBRs performed similarly and the removal averaged 94%, 90%, and 81% for benzene, toluene and xylene, respectively (Table 2.).

TABLE 2. COMPARISON OF PSEUDO-STEADY-STATE BTX REMOVAL BETWEEN FBRS

Reactor	Compound	Influent (μg/L)	Effluent (μg/L)	Removal (%)	Organic Loading Rate (kg COD/m^3-day)
BAC-FBR	Benzene	1066±303	3±2	99.7	3.8
	Toluene	1023±340	5±5	99.6	
	p-Xylene	996±340	81±53	92.0	
FBR	Benzene	834±151	45±40	94.6	2.9
	Toluene	758±380	40±40	94.7	
	p-Xylene	732±340	68±42	90.7	
BAC-FBR	Benzene	1571±303	86±40	94.5	6.0
	Toluene	1531±330	152±60	90.1	
	p-Xylene	1382±302	254±100	81.6	
FBR	Benzene	1628±142	92±52	94.3	6.0
	Toluene	1479±170	148±85	90.0	
	p-Xylene	1267±152	237±123	81.3	

After the achievement of a pseudo-steady-state at an organic loading rate of 6.0 kg COD/m^3-day, the BAC-FBR and FBR were subjected to 4-fold step-load increases for a duration of 8 hours to determine whether the use of GAC as a biofilm carrier contributed to system stability. During the increase, the removals of BTX in the BAC-FBR were 82.3%, 75.3% and 65.2% for benzene, toluene and xylene, respectively (Table 3). Under the same conditions, removals in the FBR were 64.1%, 54.7% and 46.5% for benzene, toluene and xylene, respectively (Table 3). The BAC-FBR removed 57% more COD from the influent during this period than the FBR did. The ratio of DO consumed to COD removed was lower in the BAC-FBR than in the FBR, and lower than the pseudo-steady-state value of 0.68. This indicates that the BAC carrier was responsible for the additional removal in the BAC-FBR system. Using DO consumption in the BAC-FBR to estimate biological removal, it was calculated that approximately 23% of the COD was removed COD by adsorption.

In phase two of this study, a 2" laboratory-scale BAC-FBR was operated to treat toluene contaminated groundwater. The adsorbed toluene on the BAC was monitored by collecting a small carbon sample from five different heights on the reactors. The system was fed 2.5 mg/L of toluene (an organic loading rate of 5.3 kg COD/m^3-day). The amount of adsorbed toluene on the carbon increased dramatically during the first 5 days (Figure 2.) of operation. There was no appreciable DO consumption during this period. The DO consumption increased sharply between day 4 and 11 to the maximum value

of 8 mg/L and then slowly decreased to a pseudo-steady-state average value of 5.6 mg/L. The amount of adsorbed toluene increased until day 10 and then began to decrease gradually as the degradation capability of the biofilm developed. In an attempt to assess the influence of biofilm thickness on adsorption and biological removal, a large amount of biomass was removed on day 39. Following removal, the amount of adsorbed toluene increased until the full biodegradation capability was reestablished. After the reactor resumed pseudo-steady-state operation, based upon constant DO consumption commensurate with that required for degradation of the added toluene, the concentration of toluene in the influent was increased to 11 mg/L (an organic loading of 22.6 kg COD/m^3-day). After 77 hours, the concentration was decreased to 2.3 mg/L. The amount of adsorbed toluene increased during the period of increased loading, but then began to decrease when the influent was returned to a lower level (Figure 2.). A high removal rate was achieved in all periods of operation, even during the step-load increase (99.3%, 99.4%, 95.1% and 98.5% for start-up, pseudo-steady-state, step-load and recovery, respectively).

TABLE 3. SUMMARY OF FBRs RESPONSE TO STEP-LOAD INCREASE

Reactor	Compound	Influent (μg/L)	Effluent (μg/L)	DO Consumed (mg/L)	Average Removal (%)
BAC-FBR	Benzene	7863±550	1403±280	23	82.3
	Toluene	7503±525	1850±336		75.3
	p-Xylene	6313±568	2197±340		65.2
FBR	Benzene	6918±600	2487±390	19	64.1
	Toluene	6222±610	2821±410		54.7
	p-Xylene	4911±450	2625±400		46.5

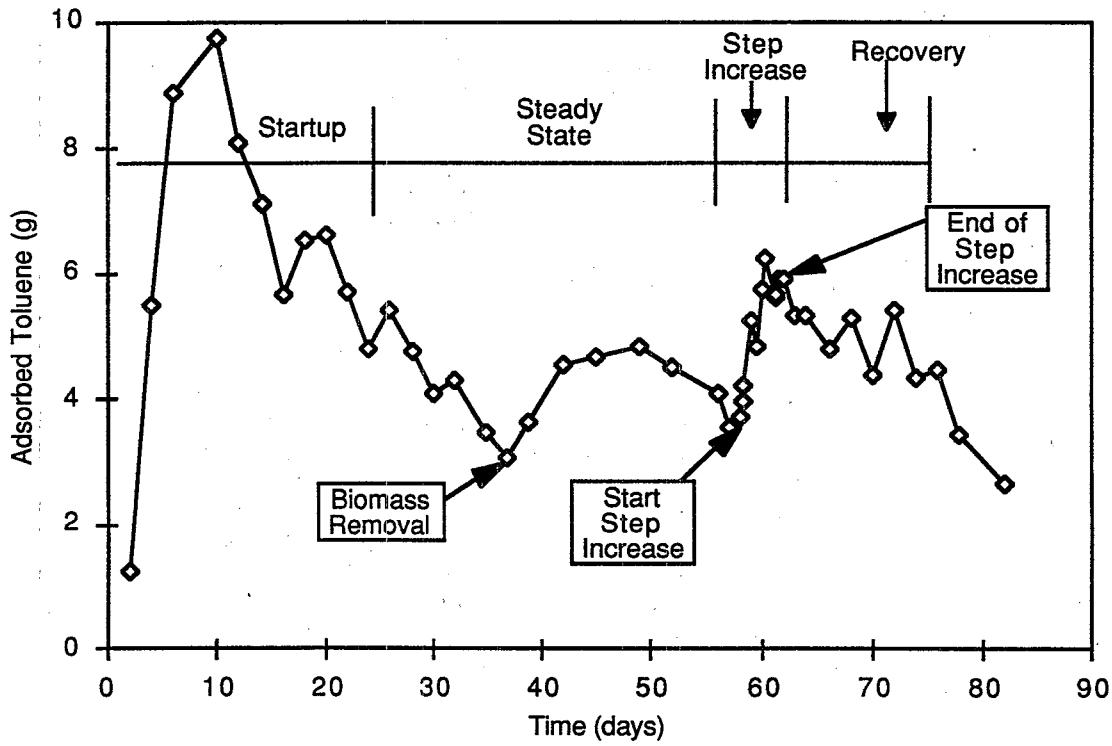

Figure 2. Total mass of adsorbed toluene in the BAC-FBR system

In the third phase, toluene contaminated groundwater (2.1 mg/L of toluene) was treated in a pilot-scale BAC-FBR. The average removal rate was 97.2% during pseudo-steady-state operation. A sample of the BAC carrier was periodically collected from the middle of the reactor and an adsorption isotherm and

analysis for adsorbed toluene was performed. The isotherm parameters were estimated using an extended Freundlich isotherm equation:

$$q_e + q_o = K_f C_e^n$$

Where: q_e is additional amount adsorbed toluene at equilibrium (mg/g). q_o is initial amount adsorbed toluene (mg/g). C_e is equilibrium concentration (mg/L). K_f and n are constants. An isotherm was also performed using clean GAC. It was found that the Freundlich K_f, which indicates adsorption capacity, decreased to approximately one-half the value found for clean carbon. This represents a substantial decrease in the toluene adsorption capacity over this period of operation.

CONCLUSIONS

Biological activated carbon systems integrate biological degradation and GAC adsorption mechanisms in a single unit process. The results from this study demonstrate the value of such an integrated approach. The BAC system exhibited a shorter start-up period than a similar biological only system and consistently maintained low concentrations of target compounds in the effluent. The performance of the two systems was similar under pseudo-steady-state conditions, suggesting that adsorption is relatively unimportant when influent concentrations are stable. Under influent loading transients, however, the BAC system maintained significantly lower effluent concentrations than the non-adsorbing system. This suggests that the activated carbon serves as a buffer to smooth out influent fluctuations and to dampen the effect of changes in the biological capability of the system. The data show that compounds adsorbed during the concentration increase were subsequently desorbed and biodegraded when the bulk liquid concentration returned to lower levels. The adsorption capacity of BAC particles decreased significantly over the course of one year of BAC-FBR reactor operation. Based upon the results of this study, several general conclusions and recommendations can be drawn.

1. At an organic loading rate of 3.8 kg COD/m^3-day and a concentration of 1.0 mg/L for each of BTX, the BAC-FBR can achieve greater than 90% removal in 3.6 min of empty-bed retention time.
2. BAC-FBR systems have a relatively short start-up period. At an organic loading rate of 3.8 kg COD/m^3-day and a concentration of 1.0 mg/L for each of BTX, the reactor can have full biological capability for the treatment of BTX contaminated groundwater within one week. The use of activated carbon as the biofilm carrier insures a high effluent quality during start-up.
3. BAC-FBR systems should provide better effluent quality during loading transients.
4. Additional DO and supplemental nutrients should be provided during a increase of substrate concentration in the influent and continued for at least 2 weeks after the increase.
5. Due to a decrease of adsorption capacity of the GAC in the BAC-FBR system, it may be desirable to periodically replace the carrier material.

REFERENCES

1. Weber , W.J., L.D. Friedman, and R. Bloom, Biologically- extended physicochemical treatment, in Advance in Water Pollution Research, S.H. Jenkin, Editor. 1972, Pergamon Press (Oxford): p. 641-56.

2. Digiano, F.A.;. Influence of biological activity on GAC performance. in Conference on Applications of Adsorption in Wastewater Treatment. 1981. Enviro Press, Nashville, Tenn. p.285-305.

3. Speitel, G.E., Jr., et al., Biodegradation of trace concentrations of substituted phenols in granular activated carbon columns. Environ. Sci. Technol., 1989. 23(1): p. 68-74.

4. Suidan, M.T., P. Fox, and J.T. Pfeffer, Anaerobic treatment of coal gasification wastewater. Wat.Sci.Tech., 1987. 19: p. 229-36.

5. Voice, T.C., et al., Biological activated carbon in fluidized bed reactors for the treatment of groundwater contaminated with volatile aromatic hydrocarbons. Water Research, 1992. 26(10): p. 1389-401.

SOIL SLURRY BIOREACTORS
BENCH SCALE STUDIES

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INTRODUCTION

The effectiveness of slurry-phase reactors to biologically degrade toxic organic compounds in contaminated solids (soils, sediments, and sludges) has been the subject of extensive evaluation studies.[1] An EPA Best Demonstrated Available Technology (BDAT) study showed remarkable pollutant disappearance rates of polynuclear aromatic hydrocarbons in creosote contaminating soil.[2] One field study has used slurried lagoons for the treatment of sludge deposits. This information tends to strengthen the claim that slurry bioremediaiton is a reliable, predictable, and fieldable technology. In spite of great acclaim, there remain some fundamental issues requiring resolution before slurry treatment matches current claims.[3]

BACKGROUND

The use of soil slurry bioreactors to treat contaminated solid materials has increased to the point that 180,000 gal.

reactors are being used as part of a remedial action plan at a waste site.[4] In spite of the continued use of slurry bioreactors, there is no generally recognized source of information to guide the operation of these reactors. As part of a general program to develop a knowledge base supporting engineering design and optimization of slurry bioreactors, we have initiated bench scale studies as a diagnostic step to aid process definition for larger scale operations.

Our research program is divided into two discrete endeavors. At a basic level of inquiry, we assess slurry reactor operation with a desire to adequately model the slurry treatment process. At a more applied level of investigation, we assess the performance of a slurry bioreactor using the best current information to select optimal operating conditions. Problems encountered at the applied level are considered for further investigation as part of the basic program.

METHODOLOGY

The slurry-phase bioreactor is a continuously stirred tank reactor (CSTR) in which contaminated solids are suspended in water. For aerobic treatment, the bioreactor is supplemented with air or oxygen, nutrients, and, where necessary, microorganisms capable of degrading the targeted pollutants. Size classification of the raw contaminated soil precedes slurry formation. The soil fraction most highly contaminated is selected for processing. Sand fractions and other non-interacting fractions are generally excluded, since they dilute the feed stream and do not contain much of the targeted pollutants. Aggressive agitation and aeration provide an environment where biodegradation of the organic contaminants is considered optimal. Limiting nutrients can be provided and physical contact between contaminants and microorganisms can be optimized in a slurry system to enhance the rate of biological reactions through improved mass transfer.

The reactors used in this study are special designs made of Pyrex glass having a total volume of 8 L and a working volume of 6 L. They are made in the general design of glass resin kettles with a four-necked cover. The reactor body has three sampling ports attached located at 5, 10 and 15 cm on the vertical dimension from the reactor bottom. The four openings in the reactor cover permit slurry loading, introduction of gas transfer lines, temperature measuring probes, and the agitator shaft. The reactors are housed in individual plexiglass chambers for spill and emission control.

The agitator attached to each reactor is powered by a 1/10 Hp direct drive, 20-1800 rpm variable speed mixer. The agitator shaft has two impellers attached to provide maximum suspension of solids. Removable stainless steel baffles provide turbulence for efficient mixing. Air or oxygen is introduced through a small gauge stainless steel tube below the lower impeller to insure the

best gas dispersion. Needle-valve flow meters permit manual adjustment of gas flow rate.

A host of operating factors are measured routinely during the operation of slurry-phase bioreactors. Our initial studies have focussed on physical limitations to mixing and the conditions of suspension required for optimal reactor operation. There are several possible mixing criteria that may be useful for slurry processing: percent suspension, suspension uniformity, off-bottom suspension, suspension height, and particle size concentration profile as a funcion of suspension height.

The bioslurry reactor was fitted with a R100 paddle at the end of the agitator shaft and an A310 axial flow impeller fitted 7.5 cm from the end of the shaft. The minimum rotational rate for complete off-bottom suspension of soil was recorded for conditions of 10, 20, 30, and 40 scfh gasflow rates and 10, 20, 30, and 40% soil solids compositions. The distance separating the impeller blades was varied and conditions for off-bottom suspension were recorded.

RESULTS

These studies showed that when the impellers are separated by 7.5 cm, air flow raised the speed of the mixer required for complete off-bottom suspension in the range of gas flow of 0-20 scfh. For flow rates of 20-40 scfh, mixing speeds required for off-bottom suspension did not increase with increased gasflow rates. These results were seen in 10, 20, 30 and 40% soil-water suspensions.

When the distance between the impellers was increased to 10 cm, the mixing speeds required for off-bottom suspension increased over the range of all gas flow rates (0-40 scfh). When the distance between impellers was narrowed to 5 cm, the speed required for off-bottom suspension were equal to or slightly less than the results for the impeller separation of 7.5 cm.

CONCLUSIONS

These studies were designed to evaluate the physical characteristics of the reactor operation leading to off-bottom suspension of the the soil slurry for the 8 L bench scale reactors. The results suggest that the conditions for off-bottom suspension are sensitive to gasflow and solids concentration in the slurry. This investigation provides a systematic evaluation of slurry mixing characteristics which will be coupled with other research studies to more clearly define the optimal operation of soil slurry bioreactors for hazardous waste treatment. Continuing studies evaluating additional controlling factors will serve as the basis of modelling slurry reactor operation.

REFERENCES

1. Ross, D. Slurry-Phase Bioremediation: Case Studies and Cost Comparisons, Bioremediation 1, 61-74, (1990/1991) Winter.

2. EPA, Technology Evaluation Report: Pilot-Scale Demonstration of a Slurry-Phase Biological Reactor for Creosote-Contaminated Soil, in print.

3. Glaser, J.A. and McCauley, P.J. Soil Slurry Bioreactors: A Perspective. Paper presented at In-Situ, On-Site Bioremediaiton: The Second International Symposium, San Diego, CA. April 5-8, 1993.

4. Jerger, D.E., Cady, D.J., and Exner, J.H., Full-Scale Slurry-Phase Biological Treatment of Wood Preserving Wastes. Paper Presented at the IN-Situ and On-Site Bioremediaiton, The Second International Symposium, San Diego, CA.,April 5-8, 2993.

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Use of Composting Techniques to Remediate Contaminated Soils and Sludges

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INTRODUCTION

As the number of sites on the EPA's National Priority List (NPL) increases (currently in excess of 50,000 identified and several hundred thousand leaking underground storage tanks) solid phase bioremediation is becoming more important for NPL site cleanup due to its cost-effectiveness. The U.S. Army recently evaluated 57 technologies for removal of contaminants in soil. Composting technology was the only innovative technology selected for development.

Traditionally, composting is the controlled, solid-phase aerobic thermophilic oxidation of organic matter by a consortia of microorganisms to yield partially stabilized residual organic matter (compost). As a result of the temperature rise, pathogenic organisms are killed.

An emerging use of composting is for the treatment of sludges and soils containing hazardous materials. In this application, the objective is to create an environment which encourages microorganisms to utilize the contaminant as its carbon source and/or electron donor. Work has recently been completed or is currently underway at Howard University for using this technology to remediate soils contaminated with pyrene, TNT and BTEX.

The pyrene and BTEX studies build upon our understanding of the catabolism of these compounds and were aimed at quantifying the parameters needed for optimization of the engineering process. The objective of the TNT studies was to develop a treatment scheme incorporating composting technology with a chemical oxidation step. The chemical oxidation step was incorporated in an attempt to overcome the lack of understanding of the catabolism of TNT. The results of these activities are described below.

MATERIALS AND METHODS

Pyrene studies were conducted using sludge from the Blue Plains Wastewater Treatment Plant (Washington, DC) and a sassafras sandy loam soil obtained from a well characterized U.S.D.A. site in Beltsville, MD. The sludge and soil were spiked with 10-15 mg/kg (dry wt. basis) of unlabeled and 15 μ Ci/kg of labeled pyrene. Previously composted sludge and wood chips were used as bulking agents. Pyrene sludge degradation studies were conducted in a laboratory scale composter developed by Sikora, et al. (1) and a series of batch composters (125 ml amber colored Erlenmeyer flask). The laboratory scale composter permitted continuous quantification of CO_2 and $^{14}CO_2$ production while the batch composters allowed the measurement of pyrene disappearance with time.

TNT studies were conducted using sludge from Blue Plains as well as aqueous suspensions in order to determine and track metabolites. All TNT studies were conducted using batch composters

Use of composting technology for remediation of a BTEX contaminated soil was site specific. A gasoline contaminated sandy soil was obtained from Sleeping Bear Dunes National Park in Traverse City, MI. The BTEX concentration in the sample received at the laboratory was very low. The soil was spiked to increase the BTEX concentration to 2000 mg/kg (dry wt. basis), which represented the higher concentration range of samples at the site. Amber colored bottles (250 ml) covered with mininert tops

were used for these studies. Because of the volatility of BTEX, other systems which did not provide leak proof conditions resulted in high losses of BTEX in abiotic samples.

RESULTS

Pyrene: During composting of a raw and limed sludge with woodchips as a bulking agent, pyrene mineralization was observed approximately eight days after the beginning of the composting period. Seventeen to twenty percent of the initial pyrene activity was recovered as $^{14}CO_2$ from a basic and neutral sludge, respectively (see Figure 1). The highest pyrene reduction achieved was 75%. A factorial design analysis of pH, temperature and moisture content based upon four experimental conditions indicated that pH and temperature had moderate inverse effects, and moisture had a moderate direct effect. The combined interaction of all the parameters produced the most significant effect (see Table 1). The target impact for the analysis was pyrene mineralization.

Figure 1. Labeled Carbon Dioxide Evolution Profiles During Pyrene Composting

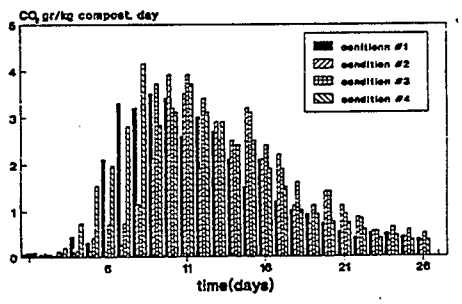


Table 1. Factorial Design and Effect Calculation of Composting Parameters

Condition No.	Factorial Conditions	Parameters pH	Moisture (%)	Temp (°C)	Pyrene Reduction (%)	Parameter Effect Calculation
1	a (high pH, low moisture and low temp.)	12	70	60	17.81	pH Effect = -0.53
2	c (low pH, high moisture and low temp.)	8	80	60	20.23	Temp. Effect = -0.36
3	b (low pH, low moisture and high temp.)	8	70	80	18.15	Moisture Effect = +0.77
4	abc (high pH, high moisture and high temp.)	12	80	80	18.14	Overall Effect = +18.74

In the soil with composted sludge as a bulking agent studies, as the amount of soil content increased the percent reduction in pyrene concentration decreases. Up to a soil loading of 30% (soil/composted sludge ratio) the percent pyrene reduction increases. Pyrene disappearance for

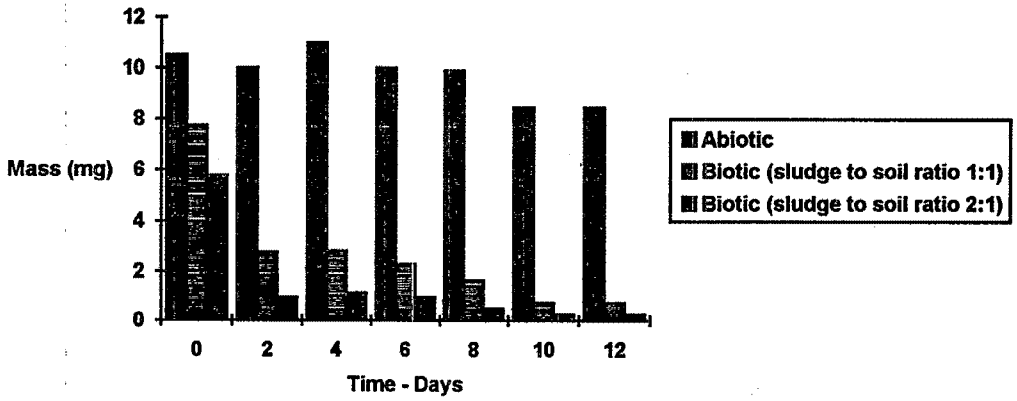
soil/sludge ratios of 0.5:1 to 4:1 fitted a first order kinetic model with k values ranging from 0.019 to 0.034 per day.

TNT: The rationale for these bioremediation studies was the chemical oxidation of TNT to trinitrobenzoic acid or picric acid and subsequent biodegradation was analogous to the transformation of BTEX and lightly chlorinated PCBs to their corresponding benzoic acid and phenols. The disappearance of TNBA to date has only been demonstrated in the batch composter with raw sludge.

Attempts to reproduce these results in an aqueous system to permit identification and quantification of metabolites have been unsuccessful.

BTEX: Ninety-three and sixty-five percent BTEX disappearance based upon head space analyses occurred in these experiments at composting temperatures of 25°C and 60°C, respectively. Because this project was site specific, only temperature and bulking agent quantity were varied. Factorial design analysis of these at low and high values, indicated temperature had a significant inverse effect, bulking agent content was significant proportionally and the combined effect was very significant proportionally. The target impact was BTEX disappearance. Figure 2 shows typical results.

Figure 2. BTEX Disappearance with Mininert at 25C Based on Headspace Results



CONCLUSION

Bioremediation using composting technology is very feasible. In cases where the biochemistry involved in the catabolism of the compounds are known, the development of engineering parameters for optimization can be obtained using a factorial design approach. The factorial design approach will not only provide information about the impact of individual parameters but will quantify the interactions of the parameters.

In cases where direct and broad based biodegradation of compounds are not yet possible, e.g. TNT. Composting technology appears to be appropriate as one of the treatment processes suitable for integration in a treatment scheme.

REFERENCES

1. Sikora, L.J., Ramirez, M.A. and Troeschel, T.A. Laboratory Composter Simulation Studies. Journal of Environmental Quality 14(3): 434-438, 1983.

FOR MORE INFORMATION

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ACKNOWLEDGMENT

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USE OF CHEMICAL DISPERSANTS FOR OIL SPILLS IN MARINE WATERS

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INTRODUCTION

Despite many precautions, oil spills into both marine and fresh waters continue to occur. Ideally, none of the spilled oil reaches the shoreline or other environmentally sensitive areas, because the slick is usually contained with booms and physically picked up with skimmers. The recovered oil is then either recycled or thrown away.

Under the best circumstances, collection efforts account for only about 10 to 15 percent of the spilled oil. Ultimately, if the oil remained in the open sea, then as much as 30 to 40 percent of it could evaporate, 50 percent could be biologically metabolized, and about 10 to 20 percent of the heaviest compounds could form tar balls or sink to mid-depths or the bottom. Within the first few days of a spill, after much of the oil evaporates, the oil becomes a thick, sticky, difficult-to-handle residue. As time goes on, it becomes even more difficult to handle. In rough seas, emulsification will also occur, leaving a water-oil "mousse" (water-in-oil emulsion) which is extremely stiff and sticky and has a volume up to five times greater than the oil alone; needless to say this mousse is difficult to remove or otherwise effectively handled.

Although they have not been used in the United States, chemical dispersants are one of the tools available in oil spill responses. Dispersants do not help in removing the oil, but promote its distribution into the water column. They can help to prevent a slick from reaching and adversely impacting sensitive areas such as wetlands or aquatic breeding areas. At best, however, only about 30 percent of the spilled oil can be "removed" by dispersants. Dispersants have been used regularly in European spills, where rougher seas often preclude use of mechanical cleanup equipment.

OIL SPILL RESPONSE CHEMICALS

As required by federal regulation, the National Contingency Plan (40 CFR 300), only chemicals that are listed with the U.S. Environmental Protection Agency may be used in U.S. waters. In 1993, forty-eight dispersant products were listed of which thirty seven were actually dispersants; the others were surface washing agents.

Dispersants enhance the natural dispersion process by facilitating the formation of small (less than 20 micron) oil droplets. When this small, the oil droplets rarely coalesce, and the dispersed oil rapidly becomes diluted in the sea water. The chemical products are surfactant formulations that have both water-compatible (hydrophilic) and oil-compatible (lipophilic) properties. With a minimum of mixing energy, the surfactants will diminish the tension at the oil-water interface and promote the breakup of the slick into small oil droplets.

DISPERSANT EFFECTIVENESS

Laboratory test results of the effectiveness of the dispersant chemicals on the NCP Product Schedule range from less than one percent to over 100 percent. Under new NCP regulations, proposed on October 22, 1993, dispersant products would have to meet a fifty percent effectiveness criterion before being listed. This is expected to reduce the number of allowable products. Since very few dispersants are stockpiled and readily available for use, only one or two dispersants will likely be used in a real spill.

Laboratory tests are routinely used to evaluate the relative effectiveness of chemical dispersants. Over 25 tests have been developed, and about six are routinely used throughout the world. Actual performance of a dispersant in a spill is not likely to be the same as that achieved in the laboratory because of application difficulties, weather conditions, and other factors. Five simplified field tests are also available, but these are not routinely used; visual observation is usually the only way to determine effectiveness in the field.

The following greatly influence effectiveness: type of oil, including chemical composition and viscosity; weathering of the oil; nature of the spill; sea state; sea characteristics, including salinity; type of dispersant, and dispersant application method.

ENVIRONMENTAL FACTORS

The decision to use dispersants always involves an evaluation of relative risks. One must weigh the tradeoffs between the potential impact to the intertidal and shoreline communities by the untreated oils (and the subsequent cleanup operation) and the potential adverse impact to water column and possibly benthic organisms by chemically dispersed oil. Although dispersants can reduce the severity of impact to fragile habitats, they may impose temporary stresses in other offshore areas because of higher short-term exposure to the toxic components of oil. Most researchers have concluded that the toxicity of modern dispersant-oil mixtures is not any greater than that of the oil alone.

Use of dispersants (commercial de-greaser) in 1967 on the Torrey Canyon spill off the English coastline lead to extensive mortalities of animals and algae, with a severely slowed natural recovery afterwards. Many concluded that dispersants should not be used under any circumstances. Since then, a number of non-toxic formulations have been developed. Under NCP regulations, products must be tested for toxicity (using the Revised Standard Dispersant Toxicity Test) and that data be published for use by spill response personnel.

There are certain environmental habitats in which dispersants should probably not be used. These include coral reefs and shallow (less than one meter depth) waters, lagoons and atolls, fish breeding areas, bird habitats, and in sensitive intertidal habitats such as mangroves and salt marshes.

REGULATORY AND ADMINISTRATIVE ASPECTS

The federal law pertaining to oil spill response actions is the Clean Water Act (CWA) as amended by the Oil Pollution Act (OPA). The National Oil and Hazardous Substances Pollution Contingency Plan, or more simply, the National Contingency Plan (NCP), was promulgated pursuant to Section 311 of the CWA to regulate all response activities.

Dispersant use requires preplanning before an incident occurs. Due to weathering, dispersants will usually not be effective if applied more than 24-48 hours after the spill starts. The preapproval plan allows for quick action in responding to specific spills. Some regional response teams (RRTs) are taking the following approach in preapproval plans: designating zones where dispersants may be used (usually the deeper offshore waters), designating zones where dispersant use may be tried (applying limited quantities, usually a barrel or two, to see if they work), and designating zones where dispersants may not be used. In almost all cases, dispersants may not be used in inland freshwater spills.

Under the NCP, regional and area contingency plans have been developed and are being updated as the plans for responding to oil spills. Under the proposed NCP regulations, RRTs and area committees must address the use of dispersants as a response option.

APPLICATION OF DISPERSANTS

One of the most critical factors in determining if a dispersant will be effective in actual use is whether it is properly applied. Two of the most significant hurdles to overcome are the lack of a dispersant supply and insufficient availability of application equipment. These should be addressed in response planning documents.

Ineffective application can result from poor mixing, use of inadequate application techniques (such as poor targeting and distribution of aerial sprays), the possibility that the oils were not dispersible, or poor formulation of the dispersant (National Research Council, 1989). Also, a major controversy concerns how to determine the field effectiveness of the dispersant.

Generally, the following principles apply: apply dispersant without dilution; ensure contact of the dispersant with the oil; apply dispersant to leading edge of the spill or at the thickest part; apply dispersants as soon as practical after the spill occurs; apply dispersant as close to the continuing spill source as possible; do not apply dispersant to oil sheen; observe the action of the dispersant from both the air and the surface; adjust application rate to achieve optimum effectiveness; and do not apply dispersants in the immediate vicinity of recovery operations. Usually, the initial response should be based on an application of 1:10 to 1:20 of dispersant to oil; this is about 50 to 100 liters per hectare (5 to 11 gallons per acre).

Aerial application is preferred to vessel application because large areas can be covered in a short time.

DECISION PROCESS FOR DISPERSANT USE

Numerous oil spill response decision processes have been described in the literature, often illustrated in the form of a decision tree. A simplified decision tree has been prepared for use by spill response personnel. The decision process should be included in the pre-spill planning documents required by NCP regulations.

PRACTICAL CONSIDERATIONS FOR DISPERSANT USE

Under the federal government's spill response policy, the On-Scene Coordinator (OSC) has limited authority to take action, unless an action involves human health and safety issues. Otherwise, various federal and state agencies must reach agreement for a decision to use oil spill dispersants. Therefore, the ground work needs to be laid in pre-spill planning documents.

Not all dispersant products on the NCP Product Schedule are equally effective. The data reported are based on laboratory analyses with a single crude oil and the results are not directly transferable to the field. Further, many dispersants show an extremely low effectiveness (less than 10 percent), even under ideal laboratory conditions.

Two considerations should guide the decision to actually use dispersants: whether there is a reasonable probability of measurable success and whether there is consensus agreement between potentially affected parties.

REFERENCE

National Research Council. 1989. Committee on Effectiveness of Oil Spill Dispersants. Using Oil Spill Dispersants on the Sea. ISBN 0-309-03882-0. National Academy Press, Washington, D.C.

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NUTRIENT APPLICATION STRATEGIES FOR OIL SPILL BIOREMEDIATION IN THE FIELD

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INTRODUCTION

During the summer of 1994, EPA, in cooperation with the Delaware Department of Natural Resources and Environmental Control (DNREC), plans to conduct a small-scale field study on the shoreline along Delaware Bay involving bioremediation of crude oil released in small quantities on 15 plots each measuring approximately 36 m^2. The goals of this research project are to obtain sufficient statistical evidence to determine if bioremediation with inorganic mineral nutrients and/or microbial inoculation enhances the removal of crude oil contaminating mixed sand and gravel beaches, to compute the rate at which such enhancement takes place, and to establish engineering guidelines on how to bioremediate an oil-contaminated shoreline. To be certain that the study is carried out properly, an engineering study is necessary to characterize the hydraulic conductivity, hydrodynamics, and nutrient flow on the selected beach. Information from such an investigation will be essential to determine the proper frequency of application of fertilizer to the plots. This paper discusses the design and conduct of such a study and presents some preliminary site characterization data. The project was conducted during the weeks of November 12 to December 3, 1993.

Several nutrient application strategies have been put forward to enable proper contact of the nutrients with the degrading microorganisms. According to hydrodynamic modeling studies conducted by researchers from Auburn University, EPA's Environmental Research Laboratory (Athens, GA), and EPA's Risk Reduction Engineering Laboratory (Cincinnati, OH) [Wise *et al.* (1993)], a strategy of nutrient application was postulated in which nutrients applied in a trench situated at the high tide line to a depth below the water table would be dissolved by the fresh groundwater and be made available to the degrading populations by the underlying freshwater lens that ebbed and flowed with the saltwater tides. This method has not been tested in the field yet. Another strategy is incorporation of a sprinkling system to apply water soluble nutrients to the contaminated site at regular intervals. This was one method used in the Alaska project, but it was not optimized from an engineering basis. Both of these methods need to be tested systematically in the field so that design guidelines for proper application and maintenance of the right amount of fertilizer to fulfill physiological needs can be developed. The method of testing in this study consisted of applying a water soluble tracer, lithium nitrate, to both plots via the trench and sprinkler methods and following the disappearance of tracer with time.

METHODOLOGY

Site Location. The location of the field study is on a sandy and slightly gravelly beach south of Slaughter Beach, Delaware. The stretch of beach used for this study was located approximately 500 m south of a locked access gate in Slaughter Beach. The surface morphology consists of a loose upper 25 mm thick layer of smooth gravel ranging in size from 4.75 mm to 19.1 mm lying atop coarse sand having a moderately homogenous particle size distribution (approximately 75% of the mass ranging in size from 0.25 to 0.425 mm in diameter). The stretch extends uniformly for 3 km and is quite homogeneous. The average distance from the low tide line to the high tide line is approximately 30 to 32 m.

Plot Layout. Two identical plots were set up as shown in Figure 1. Each plot measured 5 m by 10 m. Two types of wells were situated within and outside the vicinity of each plot: piezometers and sampling wells. The piezometers consisted of black iron rods about 2.5 m in length and 3.2 cm inside diameter

(ID). The bottoms of the piezometers were fitted with a specially made fritted brass tip that allowed water to enter the well filtered of fine sand or peat particles characterizing the deeper zone of the beach. The piezometers were equipped with pressure transducers connected to a data logger mounted to a wooden post in back of and between the plots. The pressure transducers were used to measure water head continuously to provide accurate readings of water levels during tidal cycles.

The sampling wells were constructed of stainless steel and were also about 2.5 m long. Openings of approximately 3.2 mm ID were drilled into the sides of the wells starting at 15 cm from the bottom tip and extending upward at intervals of 15 cm over a total length of 1.8 m. Stainless steel tubing of the same diameter was welded to these openings. The tubing extended inside the wells from the openings to above the tops of the wells, where plastic tygon tubing was attached for collection of water samples via syringe. The openings in the sides of the wells were covered with a fine-mesh stainless steel screen to filter out particulate matter that might clog the tubing. Thus, water samples at each depth interval were totally independent from other water samples, which enabled measurement of tracer concentrations at one depth without influence from tracer concentrations at other depths.

Tracer Application Systems. A staging area was positioned between and above the two plots. It consisted of a wooden platform supporting a gasoline-powered generator, an electric 4,200 L/h pump for delivering tracer to the plots, an 850-L Nalgene plastic reservoir containing the tracer dissolved in 800 L of fresh water, and the mounting for the data logger described above. The sprinkler system consisted of 50 mm PVC piping arranged in an H-pattern and connected to a feeder pipe leading to the pump. Sprinkler heads each rated at 400 L/h were connected to the PVC piping at the four corners of the H. The linear dimensions of the sprinkler system were 5 m x 5 m. The tracer was applied in two steps, once in the top half of the plot followed immediately in the bottom half.

Approximately 2.5 m landward from the top of each plot, a 10-m wide trench was dug by a back hoe to a depth of approximately 0.6 m. PVC piping about 75 mm ID was placed in the bottom of the trench. Holes were drilled into the pipe every 30 cm to allow uniform application of $LiNO_3$ to the bottom of the

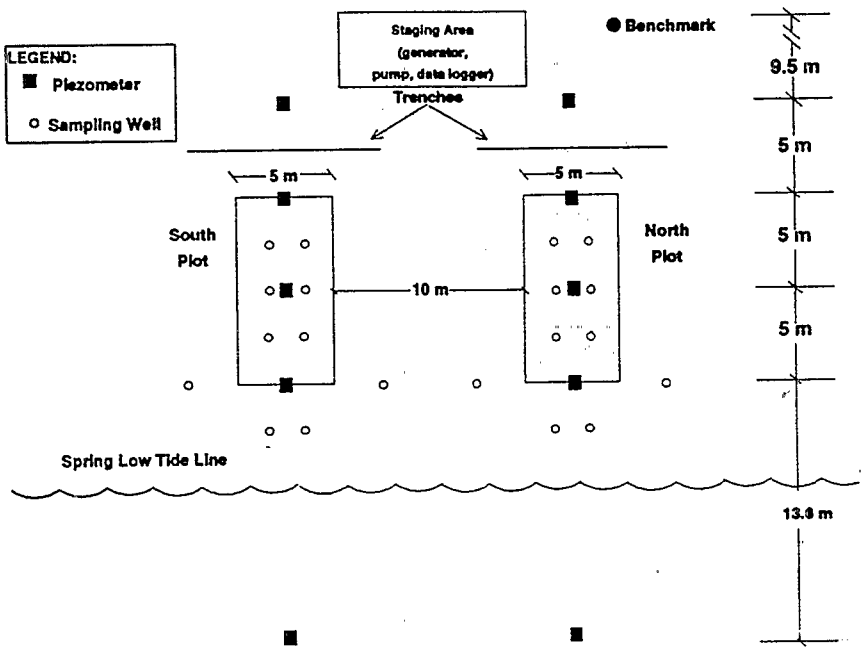

Figure 1. Schematic layout of experimental plots.

trench. After positioning the pipes in the trenches and connecting to feeder pipes coming out of the trenches, the trenches were covered over by the sand.

Application of Tracer. The original plan was to conduct two replicate experiments, one involving the trench and the sprinkler in the north and south plots, respectively, then repeating the identical experiment with the trench in the south plot and the sprinkler in the north plot. Time and inclement weather, however, precluded the second experiment. The experiment is planned to be repeated in the spring.

For the sprinkler plot, 20 kg of $LiNO_3$ was dissolved in 800 L of fresh water (the fresh water was kindly provided by the volunteer fire department of Slaughter Beach, DE). Fresh water was used to allow the density of the water after dissolution of the tracer to approximate the density of the natural salty groundwater. For the trench application, 30 kg was dissolved in the 800 L, because the trench, being 5 m wider than the plot width, required more tracer for an equivalent amount to reach the desired area of the plot. The above amounts were estimated by calculating the volume of water occupied by a wedge of beach 5 m x 10 m in area with a slope of 10% and using a sediment porosity of 30%. Computed volume was 7.5 m^3. The minimum concentration of $LiNO_3$ needed for detection in 7.5 m^3 (detection limit of about 0.1 to 0.5 mg/L) was increased by three orders of magnitude to allow for losses through dilution over time.

The tracer was added twice via the sprinkler system, once in the upper half of the plot and once in the lower half. The total time of application was approximately 22 minutes (11 minutes per plot half). Application occurred at low tide on November 22, 1993. Approximately four hours later, two hours before high tide, the tracer was added to the trench in one application. Total time of delivery was approximately 25 minutes.

Sampling. As mentioned above, small lengths of tygon tubing were attached to the stainless steel tubing protruding from the tops of the sampling wells. The tubes were color-coded and numbered to match the position of the holes along the length of the wells. Plastic, two-way, Luer-lock valves were inserted into the ends of the tygon tubing to allow attachment of 60 mL plastic syringes for collecting water samples. When samples were collected, the syringe was connected to the valve, approximately 30 to 50 mL of water was collected and wasted, then about 100 to 120 mL of water (2 syringefuls) was collected and placed into 125 mL plastic screw-capped bottles that had previously been labeled. The sampling schedule consisted of four sampling events during the first two days after application of tracer (corresponding to the two low tides and two high tides every day). Following that, sampling occurred during one low tide and one high tide daily. Samples were collected from every well at each sampling event. Some of the openings were clogged, and others at times contained no water because the water level was below the location of the opening. Approximately 1,500 samples were collected over the entire 10-day project period.

In addition to the water samples, sediment samples were collected at low tide every day. The sediment samples were collected by inserting a bulb planter into the sand, removing the column of sand from the subsurface, and placing the sand into a plastic, screw-capped, 500 mL bottle. Six sediment samples from each plot were removed each time, corresponding to the approximate locations of the sampling wells shown in Figure 1.

Analyses. Water samples were split as follows: approximately 10 mL of each water sample was poured into previously acid-cleaned, plastic, screw-capped test tubes, the test tubes frozen under dry ice, and the frozen samples shipped to Dr. Ken Lee of the Canadian Department of Fisheries and Oceans for nitrate determination. The method used was the cadmium reduction method (1) using an autoanalyzer. Another aliquot of approximately 50 mL was removed for determination of nitrate in the field by the hydrazine reduction method (2) The latter was done on only a select few samples to aid in determining approximately how much tracer was remaining at any time. The remaining 50 to 60 mL were brought back to RREL-Cincinnati for measurement of lithium by atomic absorption spectrophometry (3). The sediment samples were also brought back to RREL-Cincinnati for later measurement of lithium in the pore water remaining in the interstices of the sediment samples..

Beach Profiles. To aid in accurate measurement of beach geomorphology and its changes over time, elevation readings were collected daily at each well location on both plots. In addition, the entire beach profile was measured several times over the coarse of the 10 days of the experiment. These measurements were taken in accordance with the method of Emery (4). Two wooden profile rods each 152 cm in length marked in cm increments were used to measure elevation. A steel fence post was inserted by a sledge hammer into the ground on the vegetated dune landward of the beach. This served as a benchmark to which all noteworthy elevations were referenced. Two persons made the elevation readings. One remained at the benchmark holding a profile rod while the other stood seaward of the benchmark with the other profile rod. The distance between the two experimenters was measured by a metric tape held level between the two points. The experimenter standing at the benchmark would line up the top of the second experimenter's profile rod with the horizon and read the elevation from his own rod also lined up on the horizon. Subsequent readings were made as the second experimenter moved more and more seaward. Permanent elevation readings to the tops of all wells were made once (these readings were constant), while elevation readings at the base of the wells changed according to weather conditions and tidal flows.

RESULTS

At the time of this writing, only a limited amount of data were available for presentation in this paper. The lithium concentration measurements had only been completed for the first eight sampling events (i.e., the first 47 hours of the experiment) from the sprinkler plot. These results are presented in Figures 2 and 3 in the form of contour plots in a transect along the right side of the south plot. The Y-axis data are the absolute elevation readings (cm) of each opening in the wells. The X-axis data are the distances (m) from the top edge of the south plot to the position of the bottom two sampling wells 2.5 m below (seaward) of the bottom edge of the plot. The contours are isoconcentration lines computed (interpolated) from the measured lithium levels from the wells at various depths.

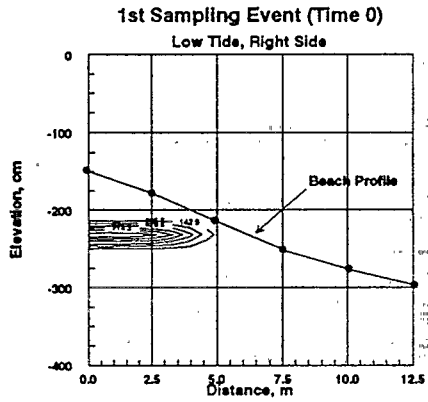

Figure 2. Isoconcentration profile of lithium in the south plot at time 0.

Figure 2 shows that most of the tracer immediately after application was centered in the top half of the plot. The highest concentration was focused approximately 80 cm below the top edge of the plot and 15 cm below the mid-point. It must be emphasized that the concentration profile shown represents the tracer concentrations measured in the water column only. Subsurface samples above the water column shown in the figure were dry, so no water samples were able to be collected. The figure does not reflect the level of tracer in the pore water within the interstices of the sand. These measurements were not available at this time. Figure 3 shows the lithium contours after the eighth sampling event (47 hours or eight full tidal cycles after application).

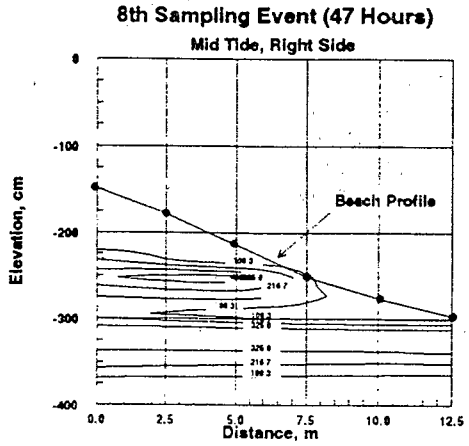

Figure 3. Isoconcentration profile of lithium in the south plot at 47 hours after application.

Clearly, the concentrations of tracer not only have not changed much even after 8 full tidal cycles have elapsed but also the tracer has spread slowly by diffusion throughout the water column to at least 2.5 m seaward from the plot. Other graphs for sampling events 2 through 7 showed approximately the same picture, with an evolving lens of tracer slowly dispersing seaward and deeper into the beach. The tracer lens tended to rise and fall with the tides. Only one sample from one of the outer wells (i.e., outside and lateral to the plot) from among all those collected during the eight sampling events was positive for lithium.

CONCLUSIONS

It is difficult to reach firm conclusions at this early stage in the analysis of the results. Only about half of the tracer results from the sprinkler plot were available at this time, none of the results were available from the trench plot, no confirmatory nitrate data had been received, and none of the critical sediment tracer analyses had been completed. Nevertheless, the little information that has been presented suggests that nutrients will likely exist for relatively long periods of time (days to at least a week or more) in a beach setting such as exists at Slaughter Beach. Tracer tends to remain in the groundwater underneath the beach surface and moves up and down with the tides. It migrates mostly in a vertical direction (landward to seaward) and does not spread laterally to a significant extent. These results should prove favorable toward bioremediation.

REFERENCES

1. American Public Health Assn. Automated cadmium reduction method 4500 F. In:Standard Methods for the examination of water and wastewater, 17th Ed. APHA, Washington, D.C.

2. U.S. EPA. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020, 1979.

3. American Public Health Assn. Direct air-acetylene flame method 3111B. In:Standard Methods for the examination of water and wastewater, 17th Ed. APHA, Washington, D.C.

4. Emery, K. O. "A simple method of measuring beach profiles. Limnol. Oceanog. 6:90-93, 1961.

BIOVENTING OF A JET FUEL SPILL IN A COLD CLIMATE WITH SOIL WARMING: A FIELD EVALUATION

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INTRODUCTION

Bioventing is the process of supplying oxygen *in-situ* to oxygen deprived soil microbes by forcing air through unsaturated contaminated soil at low flowrates[1]. Unlike soil venting or soil vacuum extraction technologies, bioventing attempts to stimulate biodegradative activity while minimizing stripping of volatile organics, thereby destroying the toxic compounds in the ground. Since the bioventing equipment (air injection/withdrawal wells, air blower, and soil gas monitoring wells) is relatively non-invasive, bioventing technology is especially valuable for treating contaminated soils in areas where structures and utilities cannot be disturbed, such as at the Hill AFB site.

The U.S. EPA Risk Reduction Engineering Laboratory, with resources from the Office of Solid Waste and Emergency Response's program, the U.S. EPA Bioremediation Field Initiative, began a 3-year field study of *in-situ* bioventing in the summer of 1991 in collaboration with the U.S. Air Force at Eielson Air Force Base (AFB) near Fairbanks, Alaska. The site has JP-4 jet fuel contaminated unsaturated soil where a spill has occurred in association with a fuel distribution network. The contractor operating the project is Battelle Laboratories, Columbus, OH. With the pilot-scale experience gained in these studies and others, bioventing should be available in the near future as a reliable, inexpensive, and unobtrusive means of treating large quantities of organically contaminated soils. This report summarizes the first 2¼ years of operation.

METHODOLOGY

Site history, characterization, installation and monitoring were summarized previously.[2,3] Fig. 1 shows a plan view of the project. Briefly, four 50 x 50 ft test plots have been established, all receiving relatively uniform injection of air. The four test plots are being used to evaluate three soil warming methods:

(i) *Passive warming*: enhanced solar warming in late spring, summer, and early fall using clear plastic covering over the plot, and passive heat retention the remainder of the year by applying insulation on the surface of the plot.

(ii) *Active warming*: warming by applying heated water from soaker hoses 2 ft below the surface. Water is applied at roughly 35°C and at an overall rate to the plot of roughly

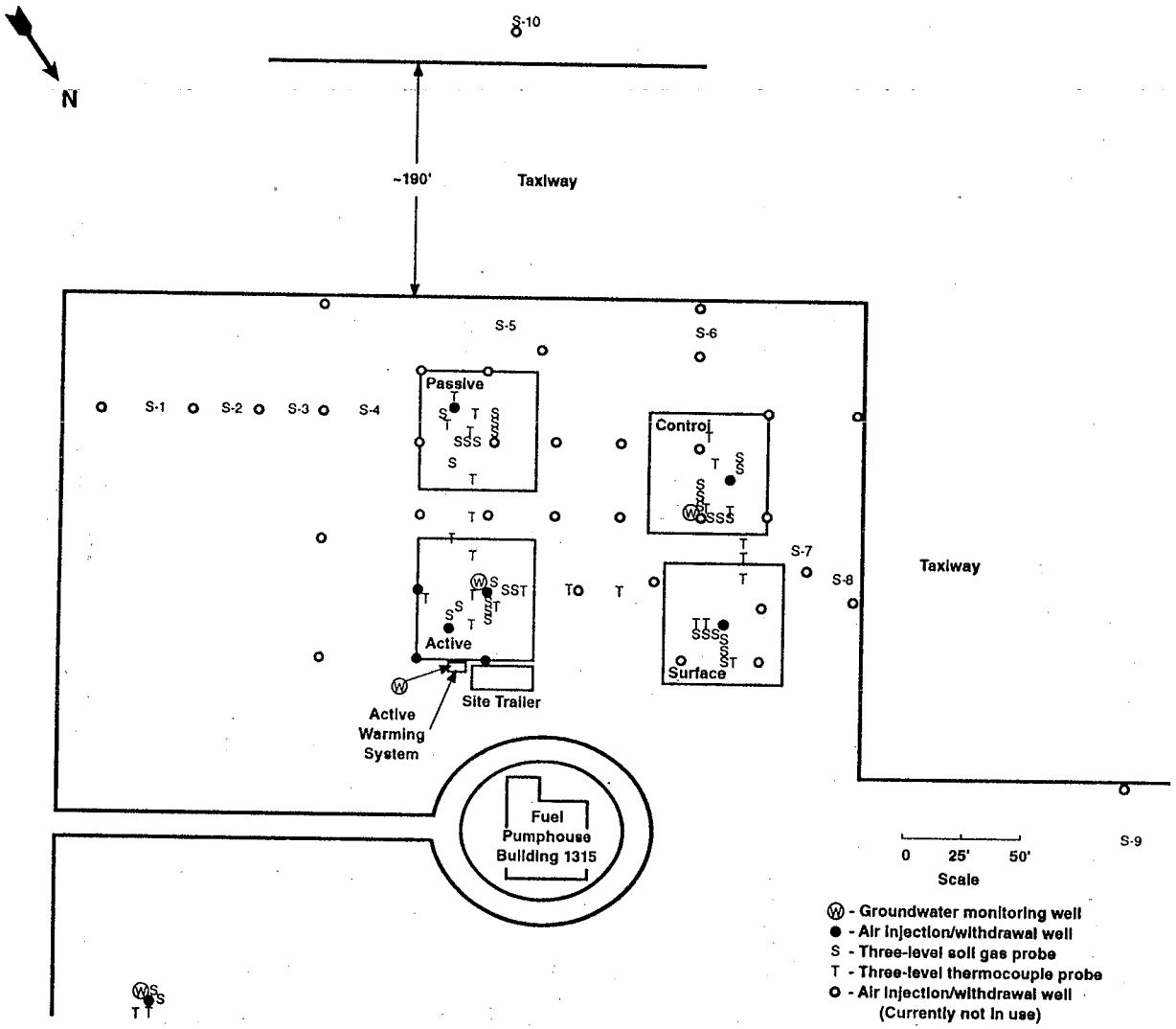

Figure 1. Plan view of the U.S. EPA/U.S. Air Force bioventing system at Eielson AFB near Fairbanks, Alaska. "S" represents three-level soil gas monitoring points, "T" represents three-level temperature probes, "O" and "●" represent inactive and active air injection wells, respectively. Instrumentation in the lower left is the uncontaminated background location.

1 gal/min. Five parallel hoses 10 ft apart deliver the warm water. The surface is covered with insulation year-round.

(iii) *Buried heat tape warming:* warming by heat tape buried at a depth of 3 ft and distributed throughout the plot 5 ft apart. The tape heats at a rate of 6 W/ft giving a total heat load onto the plot of roughly 1 W/ft^2.

(iv) *Contaminated control:* Contaminated soil vented with injected air with no artificial method of heating.

The passively heated, actively heated, and control test plots were installed in summer 1991 and the heat tape plot was installed in September, 1992. Air Injection/withdrawal wells, soil gas and temperature monitoring points are distributed throughout the site (see Fig. 1). Heating of the actively heated plot was discontinued in July 1993 in order to compare heated and unheated biodegradation rates at the same location.

Periodically, *in-situ* respirometry tests[4] are conducted to measure the *in-situ* oxygen uptake rates by the microorganisms. These tests allow estimation of the biodegradation rate as a function of time, and therefore, as a function of ambient temperature and soil warming technique. The rate of oxygen use can be converted into the rate of petroleum use by assuming a stoichiometry of biodegradation.[4] Quarterly comprehensive and monthly abbreviated *in-situ* respiration tests were conducted.

Final soil hydrocarbon analyses will be conducted in late 1993 and compared with the initial soil analysis to document actual hydrocarbon loss due to bioventing.

RESULTS

Evaluation of soil warming methods

Figure 2 displays the average temperature of each plot and at an uncontaminated background location as a function of time during the study. By applying warm water to the plot, the temperature of the actively heated plot was maintained in the range of 10-25°C compared to the contaminated (unheated) control plot where the minimum winter temperature is roughly 0°C. When heating of the actively heated plot was terminated in July 1993, it's temperature followed the temperature of the unheated control plot very closely, as expected.

The ability to control temperature in the passively heated plot was not as successful. The temperature of the passively heated plot roughly mimicked the contaminated control plot temperature except during the summer 1992 when the passively heated plot was roughly 5°C warmer than the control plot. The insulation applied during the winter has been marginally successful at best, providing 1-2°C temperature elevation in the passively heated plot relative to the control plot.

Heating by buried heat tape in the surface heated plot has been successful at maintaining between 10 and 22°C year round. The temperatures achieved in this plot in the summer were much higher than those maintained in the winter because, although the heat input was constant, the ambient temperature was much higher in the summer.

Rate of Biodegradation

The rate of jet fuel biodegradation, as estimated by in-situ respirometry tests, as a function of time for each plot is shown in Figure 3. The influence of temperature on the rate is clear: the actively warmed and surface warmed plots maintained rates 2 to 3 times greater than the unheated control plot year round. The small difference in temperature between the passively warmed and the control plots (see Fig. 2) is reflected in the small difference in the respective rates measured in these plots.

Note that the rate is non-zero (roughly 0.5 mg/Kg/day) in the unheated control plot in the middle of winter in Alaska when the average temperature of the plot is roughly 0°C (see Fig. 2). It is commonly believed that bioremediation systems should be shut down for the winter in any cold climate because it is thought the microbial activity is always zero at these low temperatures. In this case, the activity is significant.

CONCLUSIONS

The application of warm water and heat generated by electrical resistance has been successful at maintaining summer-like temperatures in the soil year round. The enhanced temperatures in the plots provided elevated rates of biodegradation. The passively warmed plot has performed only marginally better than no heating (the contaminated control) with respect to temperature and rate.

At the conclusion of this study, a cost-benefit analysis will be conducted to compare the performance of the heating methods in terms of rate enhancement versus cost of heating.

REFERENCES

1. Hoeppel, R.E., R. E. Hinchee and M. F. Arthur, Bioventing Soils Contaminated with Petroleum Hydrocarbons, *J. Indust. Microbiol.*, 8: 141 (1991).

2. Sayles, G.D., R.C. Brenner, R. E. Hinchee, C. M. Vogel and R. N. Miller, Optimizing Bioventing in Shallow Vadose Zones and Cold Climates: Eielson AFB Bioremediation of a JP-4 Spill, *Symposium on Bioremediation of Hazardous Wastes*, May 5-6, 1992, Chicago, IL. EPA/600/R-92/126, August 1992.

3. Leeson, A., R.E. Hinchee, J. Kittel, G. Sayles, C.M. Vogel and R.N. Miller (1993) Optimizing Bioventing in Shallow Vadose Zones and Cold Climates, *Hydrologiical Sci.*, 38(4), 283-295.

4. Ong, S.K., R. E. Hinchee, R. Hoeppel and R. Schultz, In-Situ Respirometry for Determining Aerobic Degradation Rates, in *In-Situ Bioreclamation*; R. E. Hinchee and R. F. Olfenbuttel, Eds. Butterworth-Heinemann, Boston, 1991, pp. 541-545.

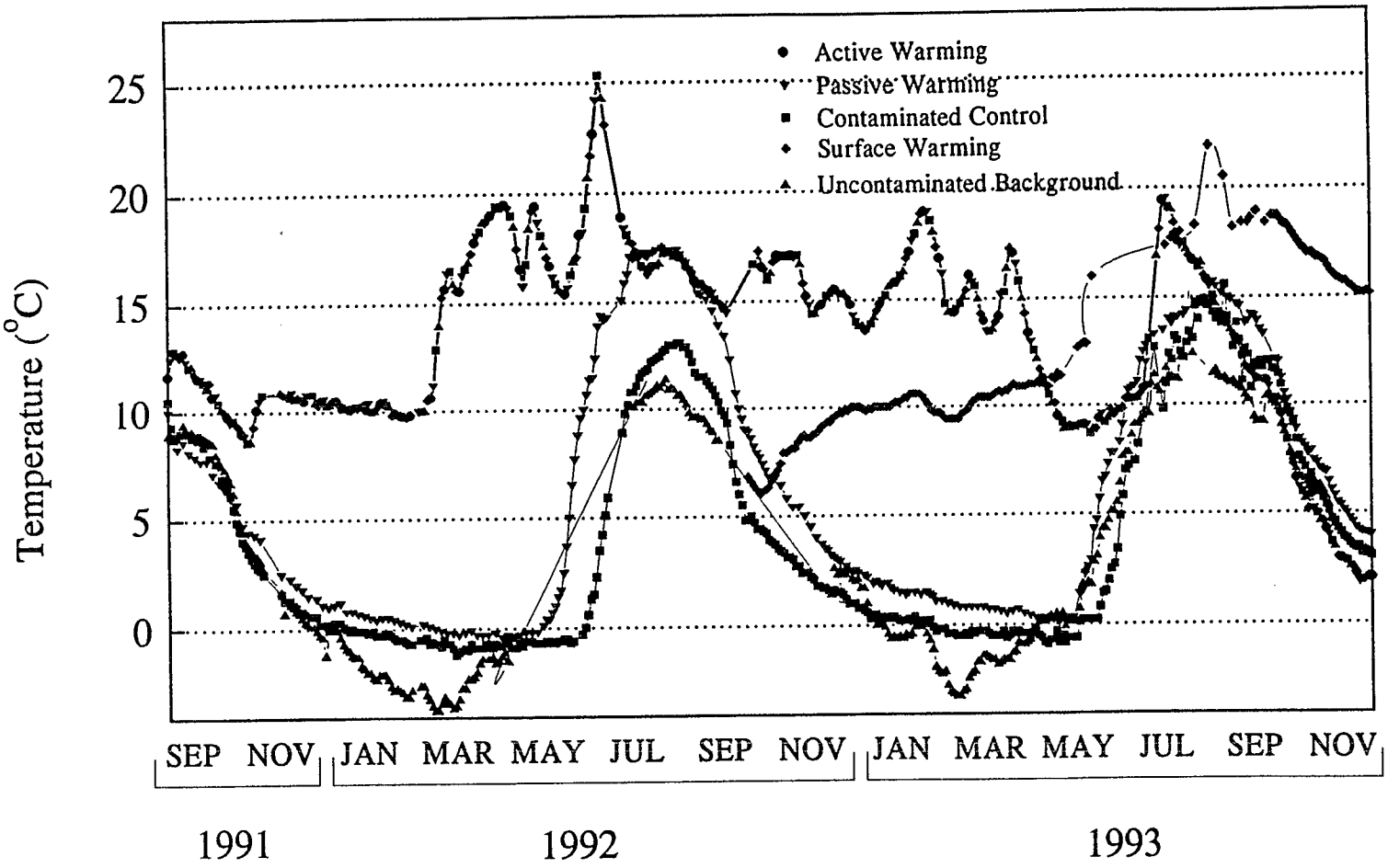

Figure 2. Average temperature of each plot and at an uncontaminated background location at the Eielson AFB bioventing site as a function of time during the study.

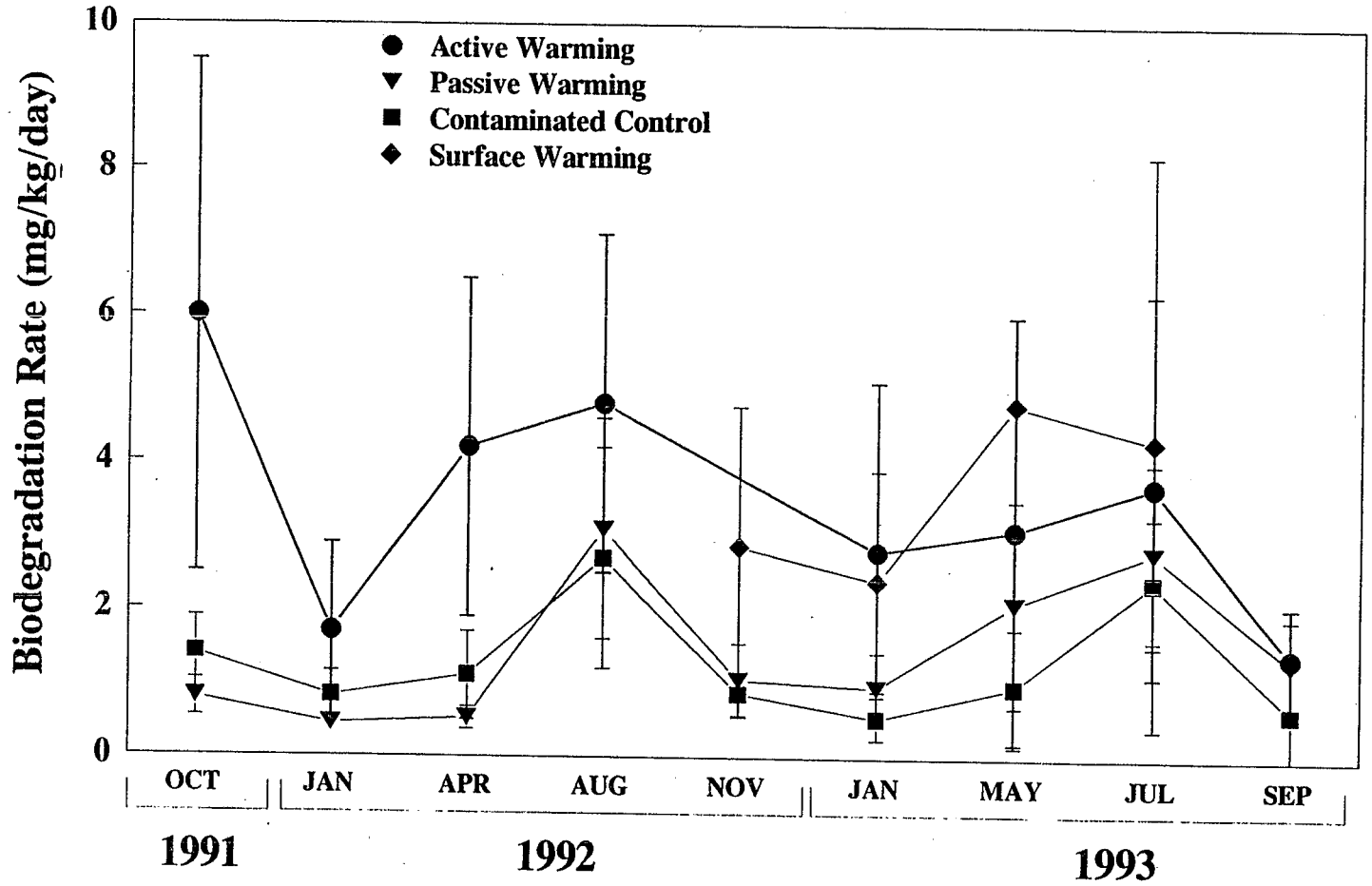

Figure 3. Average rate of jet fuel biodegradation of each plot at the Eielson AFB bioventing site, as measured by in-situ respirometry, as a function of time during the study.

SITE DEMONSTRATION OF PNEUMATIC FRACTURING AND HOT GAS INJECTION

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INTRODUCTION

Soil vapor extraction (SVE) is a method that has been found to be very effective for the remediation of soil contaminated with volatile organic compounds (VOCs) and petroleum hydrocarbons. It has gained ever increasing popularity because it can treat large amounts of soil at relatively low cost, with some estimates as low as $10 per cubic yard. This compares favorably with virtually every other remediation treatment technology, with cost estimates ranging from $80 for some forms of bioremediation to well over $1200 per cubic yard for hazardous waste incineration. Critical to the application of SVE, however, is the ability to achieve adequate vapor flow through the contaminated soil. SVE is only applicable to sites with soil types that permit the flow of contaminant vapors through subsurface formations for extraction and eventual remediation. It is necessary that air can flow through all of the contaminated soil at a site. Such vapor flow in the vadose zone depends in part upon soil characteristics such as air permeability, water content, porosity and soil homogeneity. Relative to SVE, air permeability is the measure of a soil's ability to transmit fluids based on laboratory or field airflow tests. The density and viscosity of vapors combined with the permeability of soil significantly influence the ability of the vapor to flow through subsurface strata. Permeability of soil is usually the single most important soil parameter to be considered in the successful application of SVE. It is a key parameter not only in deciding if SVE is a feasible remedial option, but also for establishing SVE system design criteria. SVE is typically more applicable to soil types with permeability values greater than 10^{-7} cm/second. This includes subsurface strata of gravel, sand, silty sand and some limestone, basalt and metamorphic rock formations. Sites consisting of igneous rock, shale, clay, dense silt, and glacial till usually are not amenable to SVE. Consequently, a process called Pneumatic Fracturing Extraction (PFE)(SM)

was developed by Accutech Remedial Systems (ARS), Inc. and was evaluated in a SITE Program demonstration to improve bedrock permeability for SVE remediation. This project was carried out under a New Jersey Environmental Cleanup Responsibility Act (ECRA) Cleanup Plan for an industrial site in Somerville, NJ where the soil and groundwater were found to be contaminated with VOCs, primarily trichloroethene (TCE). The Plan called for decontamination of the vadose zone by vapor extraction, where the formation was shale with very limited air permeability.

METHODOLOGY

The PFE process may create new or enlarge existing fractures and involves injecting bursts (10 to 20 sec) of compressed air (up to 500 psig) into narrow (2 ft) intervals of one or more wellbores. Each interval is isolated by a proprietary injector unit equipped with packers during pneumatic injection. The new fractures provide increased connections and an enlarged radius of influence, thus making vapor extraction from the vadose zone more efficient. Vapor extraction can be carried out from all wells, or with some wells either left open to allow passive air introduction or capped to direct the subsurface air flow.

The demonstration included a series of radially placed, 6-in. diameter monitoring wells, and a central 4-in. diameter fracture well that were drilled to a depth of about 20 ft. Each well was cased to about 8 ft below land surface (bls) and left uncased for the remaining depth. Pressures, extracted air flow rates, and TCE mass removal rates were compared before and after fracturing. A second prefracture test was carried out after a 24-hr dormant period to document the recharge effect commonly observed when vapor extraction is interrupted and then restarted. Samples of the extracted gas were collected using EPA Method 18 and analyzed on site by gas chromatography for TCE concentrations. These values were converted to TCE mass removal rates using the air flow rates. Surface heave during each fracture event was estimated with electronic tiltmeters.

Pressures and air flow rates also were measured while extracting individually from each monitoring well to determine whether fracturing had established connections between the fracture well and the monitoring wells and to provide information on the radius of influence created by fracturing. The effectiveness of passive air inlet was evaluated by uncapping from one to four monitoring wells while extracting from the fracture well. Pressures, air flow rates, and TCE removal rates were then determined.

A second test was also conducted because ARS is also developing a catalytic oxidation system for the aboveground destruction of chlorinated hydrocarbons, which may by investigated in a Phase II study. Accutech hypothesizes that further improvements in VOC removal rates can be achieved by injecting the hot exhaust gas (600 to 1000 °F) into one or more wells. The catalytic unit is not yet available, consequently a compressor was used in this Phase I study to produce hot air (200 to 250 °F) in order to develop and calibrate a model to evaluate the effects of injecting heated air.

Two experiments were carried out to evaluate the effects of hot gas injection. Heated air (~200 to 250 °F) was injected into a central well while extracting from one or more monitoring wells. Temperatures in selected monitoring wells were then measured. Also, pressures, air flow rates, and TCE mass removal rates were determined for the extracted air.

RESULTS

The results from the PFE tests confirmed the developer's claims. A comparison of the 4-hr postfracture data with the data from the restart test demonstrated an air flow rate increase of between 400% and 700%, averaging about 600%. Although TCE concentrations after fracturing were only slightly higher than before fracturing (58 ppmv vs. 50 ppmv, avg), when coupled with increased air flow rates the mass removal rate was increased by about 675%.

It was also found that a more complex gas mixture was extracted after fracturing, with higher concentrations of benzene, chloroform, and tetrachloroethene. Fracturing may have improved connection with pockets of these compounds, making them more accessible for extraction. Extraction at each peripheral monitoring well individually before and after fracturing confirmed that connections were significantly improved even at wells 20 ft from the fracture well, as shown by extracted air flow rates in Table 1. Attempts were made to determine whether vertical connections existed or were created by fracturing between adjacent 2-ft intervals, but the data were inconclusive, probably because of perched water in the vadose zone and the wellbore.

The results of the hot air injection tests were generally too ambiguous to confirm the developer's claims. During the first hot gas injection test (90-hr), temperatures in the monitoring wells remained essentially constant over the first 10 hours at approximately 58°F. At that time the

TABLE 1. MONITORING WELL EXTRACTION TESTS

Distance from fracture well (ft.)	Well No.	Air Flow scfm pre-fracture	post-fracture	Increase
10 s*	FMW 1	<.62#	5.15-6.36	>7.3 - 9.2
10 o/s	FMW 2	<.62-.88	6.99-5.22	>4.9 - 10.3
10 d	FMW 3	<.62	5.11-9.35	>7.2 - 14.1
10 s	FMW 4	<.62	5.7 - 8.11	>8.2 - 12.1
20 s	FMW 5	<.62	5.48-7.46	>7.8 - 11.0
7.5 d	FMW 6	<.88	4.83-7.1	>4.5 - 7.1
20 d	FMW 7	<.62	1.94-1.96	>2.1 - 2.2

* s = strike; d = dip; o/s = off strike and dip
# Some prefracture air flows are based on Accutech data.
FMW = Fracture Monitoring Well

thermocouples were raised from below 14 ft bls to 8 ft bls. Elevated temperatures were immediately observed and continued to increase over the next 10 hour before stabilizing as shown in Table 2. It is unknown whether one or more thermocouples were immersed in water in the well at the 14 feet depth.

In addition, only very low concentrations of TCE (~1 ppmv) were found in the extracted air,

both before and during hot air injection. Even with the increased air flow rates during injection, the calculated TCE mass removal rate actually decreased during hot air injection (Table 3), possibly due to changes in the subsurface air flow directions when the system configuration was changed from extraction only to extraction and injection.

A second experiment, lasting 24 hours, was carried out in another area of the site where higher TCE concentrations were anticipated. A new hot gas injection well and an additional extraction well were installed. Air was extracted from two wells, each 10 feet from the injection well. Although initial temperatures in the extraction wells were somewhat higher (~65 to 75 °F) than in the first hot gas injection test, well temperatures did not increase further in this case. Compared to an extraction-only pretest, TCE mass removal rate did increase about 50%, reflecting both increased air flow rates and increased TCE concentration in the extracted air as shown in Table 4. Perched water in the wells may explain some of the inconsistencies in the air flow rate and temperature results from the two hot air injection experiments.

TABLE 2. HOT AIR INJECTION WELL TEMPERATURES

Well	Distance from Injection Well, ft	Monitoring Well Temperature, °F			
		Initial to 10 hr @ 14 ft	After 11 hr, @ 8 ft	After 21 hr, @ 8 ft	After 89 hr, @ 8 ft
TMW2	5	59	72	77	75
TMW4	5	58	71	74	73
TMW1	7	57	75	75	72
TMW3	7	58	75	76	74
FMW4	10	57	65	70	71
FMW2	10	56	64	68	69

TMW = Thermal Monitoring Well
FMW = Fracture Monitoring Well

TABLE 3. HOT AIR INJECTION TEST RESULTS

Test	Air Flow, Inject.	scfm avg Extract.	TCE Mass Removed, lb x 10^{-6}/min
Pre-hot air	—	11.6±1.5	172±18
Hot air injection (one well extraction)	69.3±5.4	55.8±3.4	20.4±32.0
Hot air injection (four wells extraction)	73.0±3.4	82.6±7.1	31.2±10.3

TABLE 4. SECOND HOT AIR INJECTION TEST RESULTS

Test	Air Flow, Inject.	scfm avg Extract.	TCE Mass Removed, lb x 10^{-6}/min
Pre-hot air inject	—	3.7±1.8	63±27
Hot air inject (2 wells)	to 26.1*	9.2±4.7	97±33
Increase, %	—	150	54

*Some data lost due to leak in manifold; measured values ranged from 10.9 to 26.1.

Costs for the PFE demonstration were based on one year of operation, during which 1209 kg (2,600 lb) of TCE would be removed. It is estimated at $371,364, equivalent to about $307/kg ($140/lb) of TCE removed. Table 5 provides a summary of the costs and the percent each subcategory contributes to total cost.

No cost estimate was developed for the effect of hot gas injection; the planned catalytic oxidation unit was not used as the source of hot gas.

TABLE 5. OPERATING COST OF FULL SCALE PNEUMATIC FRACTURING EXTRACTION

Cost Item	Total Cost, $	Cost/lb TCE, $/lb	% of Total
Site preparation	42,000	15.79	11.3
Permitting/regulatory	1,750	0.66	0.5
Capital equipment (1.5 yr)	82,074	30.85	22.1
Startup	8,200	3.08	2.2
Labor salary	107,640	40.47	29.0
Consumables/supplies	4,000	1.50	1.1
Utilities	17,000	6.39	4.6
Emission control	70,000	26.32	18.8
Residuals (water, etc.)	37,200	13.98	10.0
Analytical services	N/A	—	—
Repair, replacement	N/A	—	—
Demobilization	1,500	0.56	0.4
Total	$371,364	139.60	100.0

CONCLUSIONS

For properly selected formations, PFE can significantly improve vapor extraction effectiveness.

The nature of the formation, air permeability, moisture content, uniformity, water table, and the presence of obstacles or potential sources of short circuits must all be considered when evaluating PFE as a remediation option.

In the demonstration, Accutech's claims were far exceeded: fracturing increased extracted air flow rates by 400% to 700% and TCE mass removal rates by almost 700% when operating with a single fracture/extraction well and no air inlet sources. With passive air inlets, the air flow rate and the TCE mass removal rate after fracturing were increased by 19,000% and 23,000%, respectively, when compared with the prefracture results. Also, the radius of influence can be increased significantly by fracturing, with 1,100% to 1,400% increases in extracted air flow rates in wells at distances of 10 feet and 200% to 1,100% even in wells at 20 feet from the extraction wells.

The estimated cost for PFE remediation of a site such as that in Somerville, NJ, is $307/kg ($140/lb) of TCE removed. Labor, capital equipment, and emissions control were the three major cost factors.

The effects of hot air injection were inconclusive. Increases in the temperature of the formation may be produced if sufficient heat is introduced, but this does not necessarily increase the TCE mass removal rate.

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CASE STUDY OF THE APPLICATION OF SOIL VAPOR EXTRACTION-AIR SPARGING TECHNOLOGY TO LEAKING UST SITE

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INTRODUCTION

Cleaning up releases of petroleum hydrocarbons or other organic chemicals from the leaking underground storage tanks (UST) in the subsurface environment is an increasing problem with over 240,000 confirmed releases. Depending on the distribution and type of contamination, cleanup of the saturated and unsaturated zones should not be considered as unrelated activities. To develop a remediation plan for selecting effective in situ treatment system(s), one must properly identify the locations and phases of contaminants.

When a nonaqueous phase liquid (NAPL) is released from a leaking underground storage tank, it will be present in 13 different phases-locations in the subsurface environment, and the most likely locations of the contaminants in the subsurface areas of a site are:

- NAPL and/or mixture of organics and water between soil particles in unsaturated and saturated zones,
- Gas phase between soil particles in unsaturated zone,
- Dissolved in soil pore water in unsaturated zone,
- Dissolved in groundwater,
- Adsorbed on soil particles in unsaturated and saturated zones, and
- Diffused into soil particles in unsaturated and saturated zones.

Mobility, a critical factor in determining pollutants transport in subsurface, is to indicate how readily individual constituent of leaked NAPL moves into air and water in the subsurface environment. It is also used for evaluating the effectiveness of in situ remediation systems in terms of abiotic processes. The primary indicators in determining mobility are vapor pressure (how easily will the contaminant volatilize into soil pore space) and solubility (what is the contaminant's affinity for water). For a recent continuous release, most of the petroleum products are likely to be in the nonaqueous liquid phase, with somewhat smaller portions existing in the vapor and dissolved phase but will increase over time. On the other hand, a large portion of the weathered petroleum hydrocarbons have already evaporated in soil vapor and dissolved in pore water and groundwater with residual fractions being sorbed on and diffused into soil/rock particles. The latter two phases would be less mobile but may act as a continuing source over a fixed time.

Soil vapor extraction-air sparging (SVE-AS) systems combine in situ aeration of groundwater with vacuum enhanced recovery of hydrocarbon-laden vapors that are present in the unsaturated zone. The injection of air into the saturated zone functions both to volatilize residuals of petroleum hydrocarbons and to increase the dissolved oxygen concentration in groundwater. Enhancement of dissolved oxygen may in turn promote biodegradation by increasing the population of indigenous microbes. Because of the dual action of sparging and soil vapor extraction, under certain geological conditions and proper engineering design, the system may provide effective means for immediate abatement of dissolved contaminants in the saturated zone and contaminant vapors in the unsaturated zone.

Figure 1 presents a schematic diagram of these processes. As shown in this figure, air is sparged into the groundwater, promoting partitioning of volatile organic compounds into the soil pore spaces within the sparged air streams. The air streams rise to the groundwater table, and the released hydrocarbon-laden air is removed by the SVE system. If volatile hydrocarbons are present in the unsaturated zone, the SVE system will also function to remove these compounds by volatilization and advection. Many practitioners claim to effectively remediate hydrocarbons contaminated soils in both saturated and unsaturated zones by using SVE-AS system, however, limited performance data support their claims.

This paper presents an approach for evaluating the effectiveness of SVE-AS technology with an actual leaking UST case study that system evaluations are being conducted at the site. The site is located in Cleveland, Ohio and evaluated by a joint effort by the BP Oil Company, the Ohio State Fire Marshall Bureau of Underground Storage Tank Regulations, U.S. EPA Region V Office of Underground Storage Tanks, and U.S. EPA Risk Reduction Engineering Laboratory. A site specific Quality Assurance Project Plan (QAPP) was developed by the EPA to ensure the validity of data collected from an existing SVE-AS system installed at the site.

METHODOLOGY

1. Case Study Site Description - An SVE-AS system has been installed and operated at an active gasoline retail-service station as indicated in Figure 2. The surrounding area is largely residential, with light commercial development. Geologically, the site is located upon the Eastern Lake and Till Plains of the Central Lowland Province. The soil is composed of sandy loam, silt, and clay and is characteristic of a remnant beach ridge. Depth to first groundwater table at the site is approximately 19 feet below grade.

Groundwater flow direction is towards Lake Erie to the north. The groundwater gradient at the site is approximately 0.04 foot/foot. In situ aquifer testing has not been performed at the site. Based upon the lithology, the site hydraulic conductivity is likely to be highly variable.

The current system operation provides remediation across the east half of the site. The locations of SVE-AS wells, monitoring wells, and soil borings are indicated in Figure 2

2. SVE-AS Processes Evaluation Experimental Design - For the purpose of the initial remediation activities at the site, the radius of influence for each vapor extraction well was projected to be 30 feet, and the radius of influence for each air sparging well at 15 feet. The system was designed such that the influence of the air sparging well would be encompassed completely by the influence of the extraction well. The well configuration consists of two remediation cells. Each cell contains one central SVE well surrounded by three air sparging wills.

The SVE portion of the remediation system consists of two SVE wells manifolded to a 5-horsepower regenerative blower. The SVE wells are constructed of 10-foot sections of 4-inch PVC continuously wound well screen. Twenty-two vapor monitoring points were installed on site to monitor the area of influence of both the air sparging and soil vapor extraction systems.

The AS portion of the remediation system consists of six air sparging wells manifolded to a 15-horsepower, oil-free air compressor. Air sparging monitoring wells provide data used to determine the operating effectiveness of the AS system.

3. SVE-AS System Performance Monitoring - The purpose of monitoring is to determine the amount and movement of pollutants in the subsurface environment before, during, and after remediation. An effective monitoring program includes the design of a reliable well network to ensure a complete determination of and assessment of the site conditions.

Vapor monitoring - To evaluate the performance of the SVE-AS systems, periodic field sampling and data collection activities are necessary. Vapor monitoring of the remediation system at the site is conducted at the SVE wells, vapor monitoring points (VMPs), and the SVE stack emission.

Groundwater monitoring - Groundwater monitoring at the site is performed at the groundwater monitoring wells (MWs) and the air sparging monitoring wells (ASMs).

Soil Sampling - Three soil sampling events are scheduled to be collected during the field demonstration activities. These samples are collected and analyzed for BTEX and TPH. Results are compared with the samples collected prior to the system start-up and at the conclusion of the field evaluation to assess the effectiveness of the technology for removing contaminants from the soil.

4. SVE-AS Systems Operation Monitoring - Several process control parameters are periodically measured to determine the adequacy of system operation as follows:

Soil vapor flow and temperature,
Ambient conditions (air temperature and barometric pressure),
System vacuum/pressure,
Soil vapor Oxygen and Carbon Dioxide,
Soil vapor volatile organic compounds,
Injection air pressure and flow rate,
Groundwater table elevation,
Groundwater dissolved oxygen,
Groundwater temperature, conductivity, and pH.

RESULTS

1. Soil Vapor - After two years of operation, the vapor concentrations from all four extraction wells have began to reach asymptotic mass removal rates. Since January 1993, the average constant levels of total BTEX/TPH from VEW-1, VEW-2, VEW-3, and VEW-4 were 20/200, 10/50, 4/10, and 10/60, respectively.

2. Groundwater - Results from laboratory analyses indicated TPH levels in the groundwater samples were reduced from 40 mg/l (ppm) to below laboratory method detection limits during the first two months of air sparging operation. Total BTEX concentrations reduced from as high as 650 ppb to less than 3 ppb in January 1992, and the concentrations have been maintained at these levels with intermittent operation of SVE-AS systems.

3. Soil - A preliminary assessment of the SVE-AS systems performance in terms of changes contaminant levels in the subsurface soils in silty clays in the unsaturated zone was made by comparing of soil samples collected in three different stages (i.e. August 1991, October 1992, and August 1993). Contaminants concentrations in soil samples varied considerably throughout the site. The average values of total BTEX/TPH concentrations in the initial soil samples ranged from 15/280 to 420/140 ppm with the highest reading of 1088/320 ppm from the VEW-1 vicinity. After 13 months of SVE and 12 months of AS system operation, soil borings were collected, and the measured BTEX/TPH levels were in the range of 0.54/62 to 30/63 ppm. However, in the August 1993 soil sampling survey, the averaged values of BTEX/TPH ranged 0.005/42 to 228/125 ppm in the clay-rich soils in the unsaturated zone.

CONCLUSIONS

Based on initial results, hydrocarbons levels in the subsurface vapor and groundwater have been decreased to below detection limits. However, contaminants concentrations in soil samples have decreased substantially from initial concentrations but have not reached the State cleanup levels. In

addition, contaminants concentrations varied considerably due to the complexity of lithology of the site. All the data obtained during the two-year monitoring program are being evaluated.

ACKNOWLEDGEMENT

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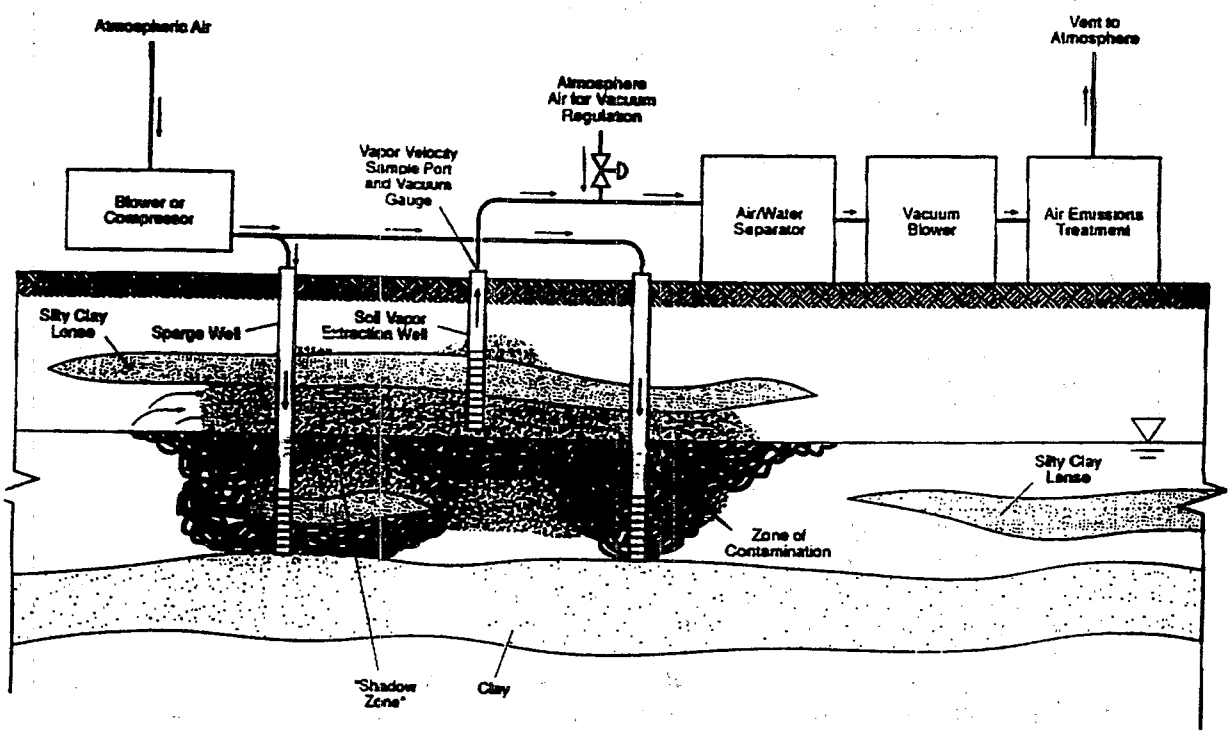

Figure 1 - Soil Vapor Extraction-Air Sparging System Schematic

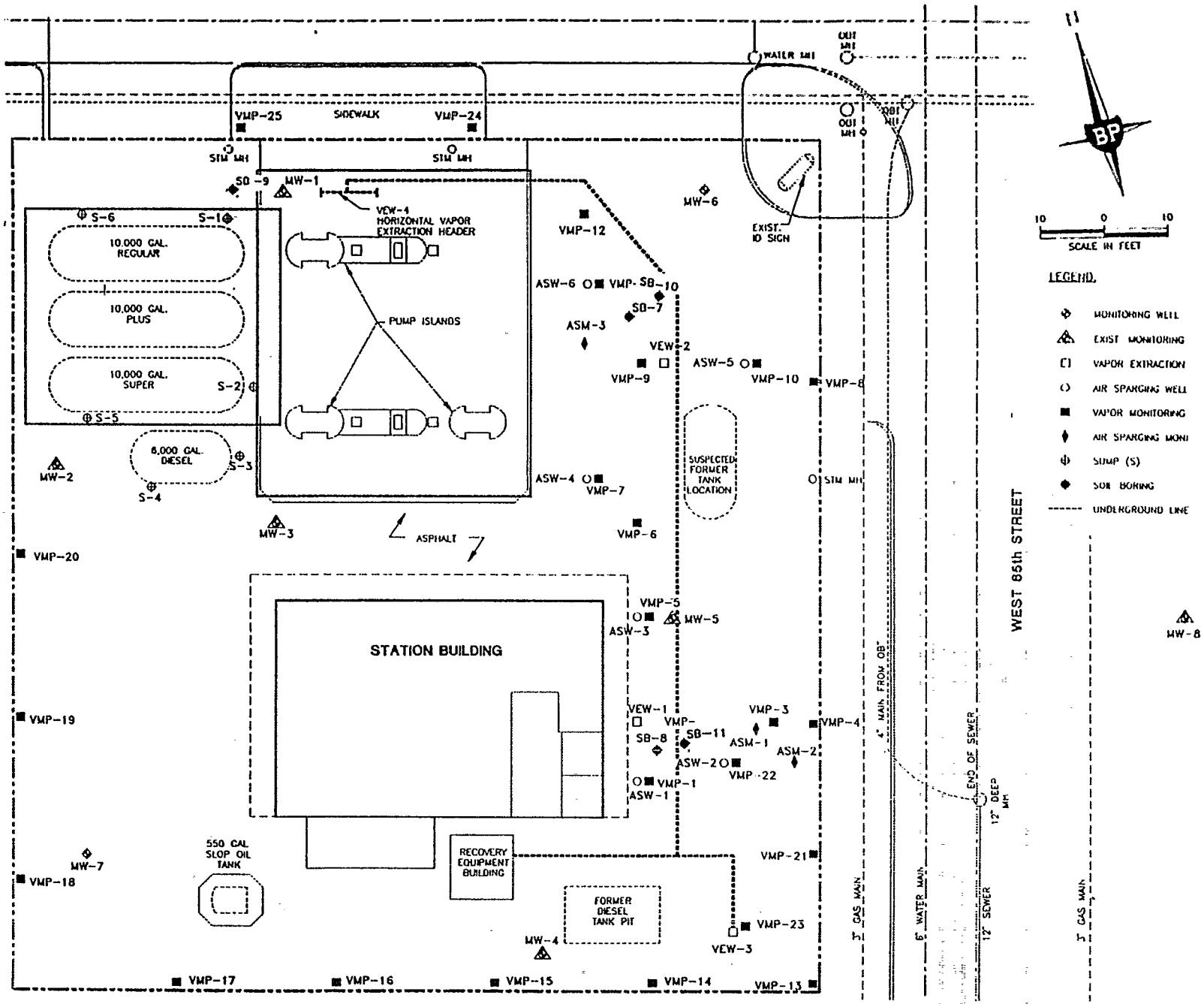

Figure 2 - Site Plan (From BP Oil Site Evaluation Report, 1993)

PARTICLE SEPARATION (SOIL WASHING) PROCESS FOR THE TREATMENT OF CONTAMINATED SOILS

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INTRODUCTION

Warren Spring Laboratory has developed a soil separation and washing process under the SITE Emerging Technology Program. This paper describes pilot scale test work conducted on soil at a gas works that was contaminated with PAHs, petroleum hydrocarbons and heavy metals. The soil from the gas works was investigated in the laboratory to characterize the distribution of contamination on the basis of soil particle size, density, magnetic susceptibility and hydrophobicity (1, 2, 3, 4). This information was then used to design the pilot scale flow sheet.

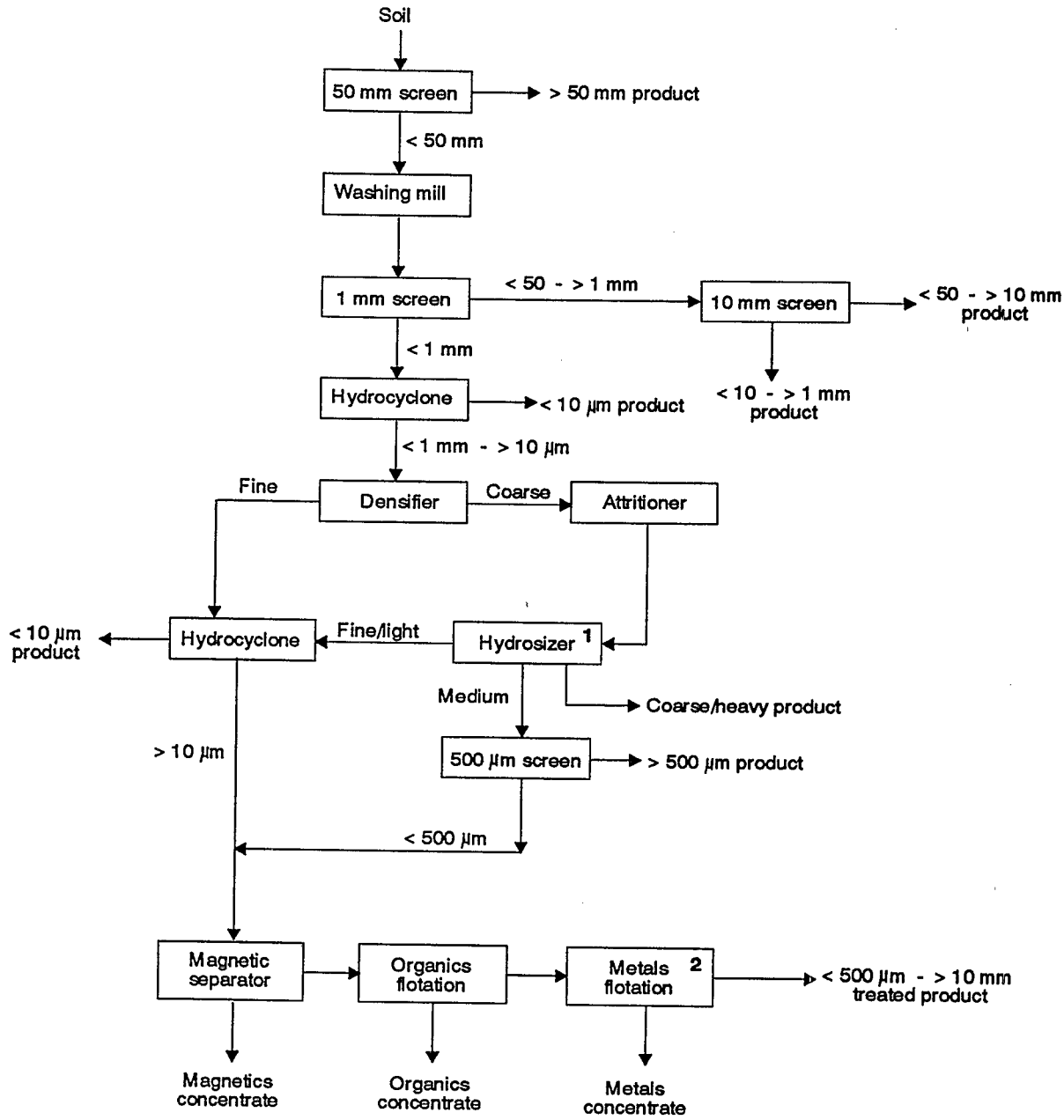
The main contaminants in the soil were: arsenic (> 30 mg/kg), lead (> 800 mg/kg), PAH (<200 mg/kg) and petroleum hydrocarbons (> 600 mg/kg).

METHODOLOGY

The pilot scale circuit was operated for a period of some four weeks. The nominal throughput rate was 1 ton per hour with about 40 tons being treated. The soil was treated as a water based slurry with minimal reagents used as additives. The overall flowsheet that was tested is shown in Figure 1. This includes all of the various options that were investigated. The major operations involved are size separation, washing and attrition, separation based on combined size/density differences, flotation and magnetic separation. The contaminated soil is initially screened at 50 mm under high-pressure water jets. The jets help break up any agglomerated material and wash off adhering fine particles from coarser particles. The > 50 mm material is anticipated to be a clean gravel product.

The < 50 mm material enters a washing mill containing granite boulders. Here further washing takes place, and the boulders assist in the breaking up of any clay balls. The overflow from the washing mill is screened at 1 mm again under a water jet to remove any adhering fine particles from coarser particles. The < 50 - > 1 mm material is then further screened at 10 mm to produce two products: < 50 - > 10 mm, which is expected to be a clean fine gravel; and a < 10 - > 1 mm product containing some contaminated carbonaceous (primarily coal/coke) particles, which will be stockpiled for further treatment by jigging. Jigging is a process by which particles of different specific gravity undergo vertical stratification.

The < 1 mm material passing the 1 mm screen enters a primary hydrocyclone operating to separate at approximately 10 μm. The overflow from this hydrocyclone will be a highly contaminated fine (< 10 μm) product which will require further treatment (for example by bioslurry treatment) or



1 Alternative option is to use spiral classifier
2 Alternative option is to use multi-gravity separator

Figure 1. Pilot Test Flowsheet for Treatment of Gas Works Soil.

disposal. The underflow from the hydrocyclone will be < 1 mm - > 10 μm and enters a spiral classifier operating as a densifier. The densifier stage is necessary in order to increase the solids concentration of the coarser material entering a later attrition stage. Any fines incorporated in the water removed at the densifier stage enter a secondary hydrocycloning stage.

Within the attrition scrubber the attrition action will remove any surface contaminants from the coarser particles. Dispersants are added to maintain removed contamination in suspension and to discourage the finer particles from re-adhering to particle surfaces. Following attrition, the material undergoes a separation stage based on the combined parameters of size and density. Both a spiral and a hydrosizer were investigated. With a hydrosizer, three product streams result: a stream with the coarsest and heaviest particles; a stream with the finest and lightest particles; and a stream with particles of intermediate density and size. The coarse and heavy particle stream from the hydrosizer will essentially be coarse sand and will be stockpiled. If chemical analysis shows this material is not sufficiently clean then more treatment by a further gravity separation process may be necessary.

The fine and light particle stream from the hydrosizer will consist primarily of fine particles of clay and contaminant liberated by the attrition process and also lighter (but possibly larger) carbonaceous particles that may have adsorbed organic contamination. However, as the separation principle of a hydrocyclone does not result in products of a definite specification, then some of the particles in this stream will be transitional in size/density with the particles in the intermediate stream. Consequently, as it may be possible to clean these particles by flotation, the fine and light particle stream is taken to a secondary hydrocyclone (where it is combined with the fines from the densifier) so that they can be removed as underflow prior to disposal of the overflow as a contaminated fine product that will require further treatment or disposal. It is not sensible for the fine material to undergo a floatation process, because excessive fines require large quantities of reagents. The fines can also coat large particles, thus inhibiting collector attachment to particle surfaces.

The stream from the hydrosizer with particles of intermediate density and size will include particles of similar hydraulic density but varying physical properties. For example, some particles may be relatively larger but lighter (e.g. coke or other carbonaceous material that may have high levels of contamination) while other are relatively smaller but heavier. Consequently, as tests have shown that material > 500 μm is difficult to float successfully, this stream is screened at 500 μm to remove any remaining > 500 μm particles as a contaminant concentrate for further treatment or disposal.

The < 500 μm material from the screen is combined with the underflow from the secondary hydrocyclone. More dispersant is added to minimise the coating of larger particles by smaller particles and so avoid any adverse effects on the performance of the remaining processes. This material then enters an optional stage of magnetic separation where a heavy metal contaminated product may be removed that may be suitable for recycling. Or it may enter directly into a flotation stage designed to remove organic contamination. At this flotation stage, a collector reagent is added to remove selectively organic contamination as a froth concentrate for further treatment or disposal while the remainder of the material proceeds to the final process.

The final process needs to treat any metals remaining in the material, and both flotation and a gravity separation process (using a multi-gravity separator) were investigated. With flotation, another collector reagent is added to remove selectively metal contaminants as a froth concentrate for further treatment or disposal while the remaining material represents the treated product.

RESULTS

Samples of process streams were collected around the circuit to make possible a mass balance of both contaminants and soil. All products were included in this sampling regime. These products are:

* > 50 mm clean gravel product
* 10 - 50 mm clean fine gravel product
* 10 - 1 mm product that may require further treatment by jigging
* < 10 μm contaminated product from the hydrocyclones that may be treatable by bioslurry process
* < 1 mm coarse sand from the hydrosizer that may require further treatment by gravity separation
* < 1 mm - > 500 μm contaminated light gravity concentrate from screen after hydrosizer
* froth concentrate with organic contamination
* froth concentrate with metal contamination
* magnetic concentrate with metal contamination (optional)
* < 1 mm treated material.

At the time of this writing, the results of chemical analysis are still coming in. Data reduction and evaluation will provide a material balance around the complete flowsheet for soil, individual contaminants, and process water. This will enable performance determination for the complete process as well as for individual unit operations. Additionally, the percentage removal for each contaminant in any clean products will be determined by comparison with the original soil.

REFERENCES

1. Wood, P. and Pearl, M. Characterisation and Treatment of Contaminated Soils using Mineral Processing Techniques. In: Nineteenth Annual RREL Hazardous Waste Research Symposium - Abstract Proceedings. EPA/600/R-93/040, U.S. Environmental Protection Agency, Washington, DC, 1993, 192-196.

2. Pearl, M. and Wood, P. Separation Processes for the Treatment of Contaminated Soil. In: Contaminated Soil '93. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1993, 1295-1304.

3. Pearl, M., Wood, P., Martin, I., Barber, S., LeJeune, G. and Bardos, R. Particle Separation Techniques for the Treatment of Contaminated Soils. Third Annual Symposium on Groundwater and Soil Remediation. BIOQUAL, Quebec, 1993, 269-284.

4. Pearl, M., Wood, P., Martin, I., Barber, S., LeJeune, G. and Bardos, R. Using Separation Processes from the Mineral Processing Industry as an Enabling Technology for Soil Treatment - Laboratory and Pilot Plant Study: Interim Report. Presented at: International Conference of the NATO/CCMS Conference on 'Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater' Phase II, Quebec City, September 1993.

SITE PROGRAM DEMONSTRATION OF IN SITU STEAM ENHANCED RECOVERY PROCESS AT THE RAINBOW DISPOSAL SITE IN HUNTINGTON BEACH, CALIFORNIA

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TECHNOLOGY DESCRIPTION

Steam Enhanced Recovery Process (SERP) is designed to remove volatile compounds such as halogenated solvents and petroleum hydrocarbons, and semivolatile compounds from contaminated soils *in situ*. The vapor pressures of most contaminants will increase by the addition of steam, causing them to become more volatile and mobile. The technology operates through wells drilled in the contaminated soil. Injection wells deliver high pressure steam (15 psig, 90% dryness) to the soil, while extraction wells draw a vacuum on the soil. The pressure gradient drives the steam, water, and vaporized contaminants to the extraction wells where they can be removed for disposal or recycling. Figure 1 illustrates the operation of the process beneath the soil surface.

A site to be treated with *in situ* SERP must have predominantly medium to high permeability soils. A geological confining layer below the treatment depth and a confining layer above the treatment zone help to contain the flow of steam. Injection and extraction wells are arranged on the site in a pattern designed to promote even distribution of the steam. Site-specific factors determine the number of wells used, their arrangement on the site, their construction, and the above-ground process equipment to be used.

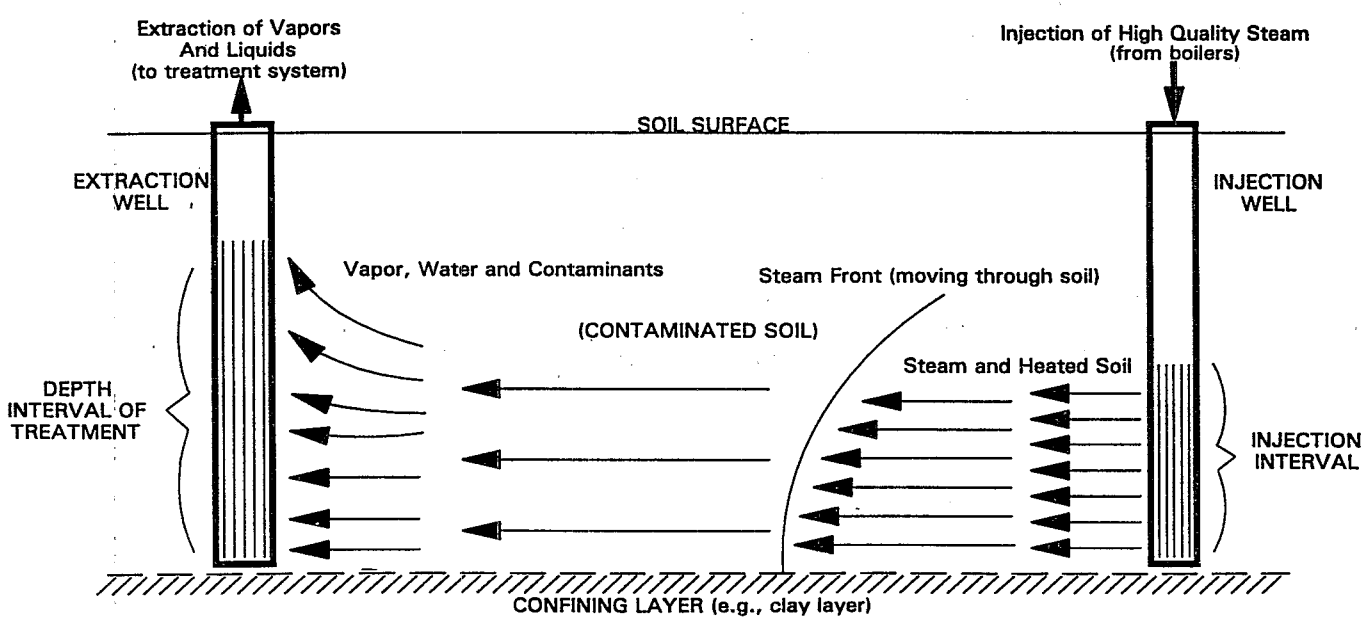

Figure 1. Conceptual Operation of SERP Below the Soil Surface

A full-scale SERP system with thirty-five injection wells and thirty-eight extraction wells was used to treat an acre of soil up to 40 feet deep at the Rainbow Disposal site in Huntington Beach, California. This site was contaminated with diesel fuel compounds. Figure 2 shows the above-ground process equipment used for the SERP system. Water for steam generation was pumped from an on-site deep water well, treated by ion exchange and the addition of chemicals, and heated in one of two natural gas-fired steam boilers. High pressure steam was delivered to all the injection wells using a manifold system. Air-lift pumps were used to remove accumulated oily water from the extraction wells, and a vacuum pump maintained a negative pressure on the soil and removed the vapors from each extraction well.

Heated liquids (condensate) from the extraction wells were routed to a heat exchanger used to pre-heat the boiler feedwater and then treated in a gravimetric oil/water separator. The oily product from the separator was collected in a storage tank. The remaining water was then treated further using filtration and activated carbon before being discharged directly to an underground sewer. Liquids entrained in the extracted vapors were removed using a knock-out drum. The vapor stream was then treated in a thermal oxidizer unit which used electrical heating to oxidize the vapors before discharging them to the atmosphere through a stack.

The full-scale SERP system used at the Rainbow Disposal site was operated for approximately two years. The system was operated for 16 hours a day, 5 days a week for the first year. Twenty-four hour operation, 6 days a week was used for the remaining year. During most of the treatment, steam injection and vacuum extraction were used simultaneously. Vacuum extraction alone was used when the boilers were inoperable, during interim soil

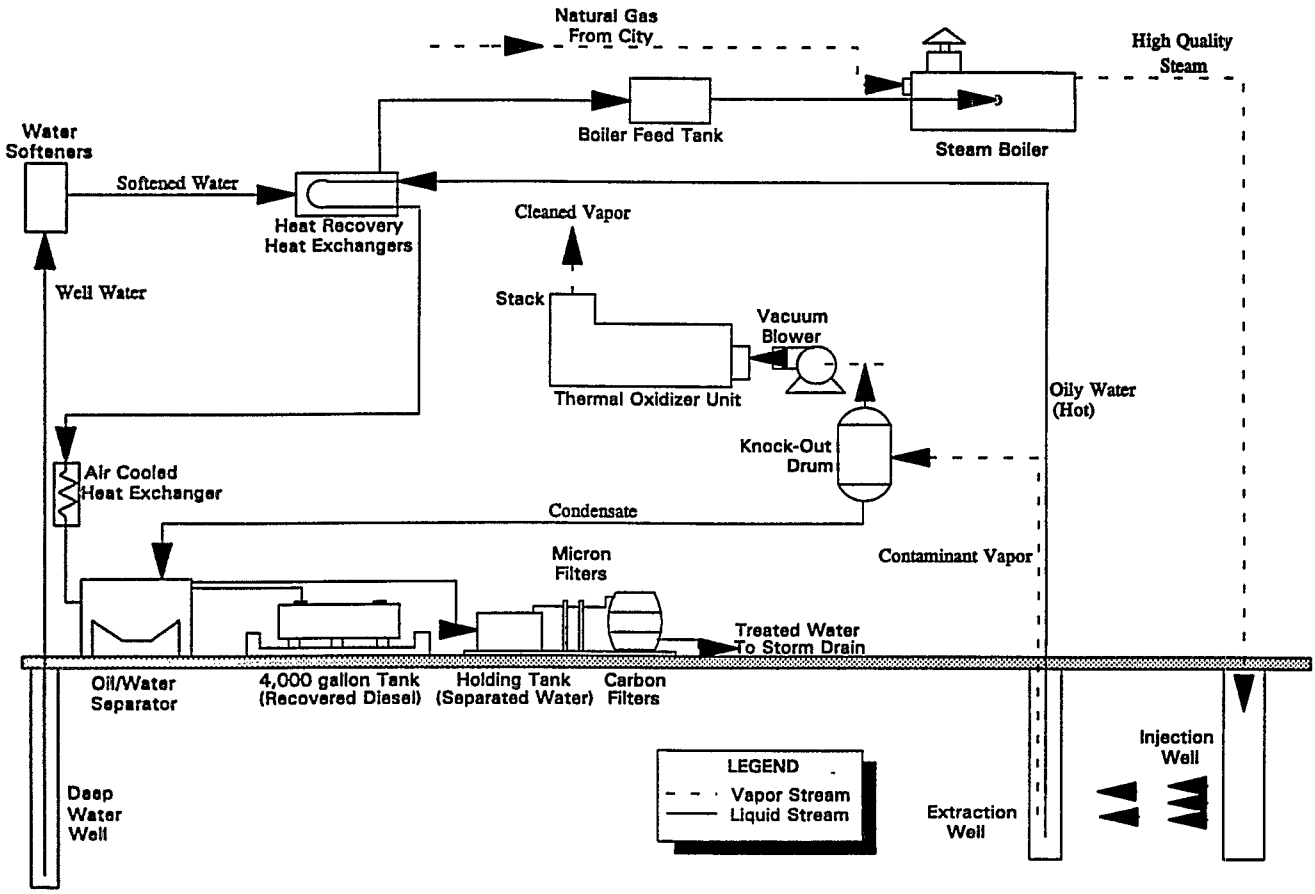

Figure 2. The SERP Process Treatment Train

sampling activities, and at the end of the remediation. Vacuum extraction alone after steam injection is expected to dry and cool the soil and remove contaminants from lower permeability soils.

DEMONSTRATION METHODOLOGY

The U.S. EPA Superfund Innovative Technology Evaluation (SITE) Program became involved with the *in situ* SERP technology developer after the system was installed on the Rainbow Disposal site. Pre-treatment soil sampling and analyses occurred prior to full SITE Program participation. Therefore, the focus of the Demonstration was on the condition of the soil after treatment to determine if the technology met the site-specific cleanup criteria of 1,000 ppm of total petroleum hydrocarbons (TPH, diesel). An economic analysis of the system was also a primary objective for the Demonstration.

Before treatment, one to four samples from each of twelve boreholes within the defined perimeter of contamination were sampled by the technology developer and analyzed for TPH. Some of the soil samples were also analyzed for benzene, toluene, ethylbenzene, and xylenes (BTEX), and semivolatile organics. The pre-treatment results will be used by the SITE Program in a non-critical evaluation of the removal efficiency of the treatment.

The SITE program (EPA) performed post-treatment soil sampling and analyses, including sampling from boreholes adjacent to (within four feet) and at the same depths as those sampled before treatment. Additional samples at other depths were collected in most of these boreholes. Twelve additional boreholes were also sampled, including six outside the defined perimeter of contamination for a total of 24 boreholes. Samples collected after treatment were analyzed for TPH, BTEX, and total recoverable petroleum hydrocarbons (TRPH). Six sets of triplicate samples were collected at randomly determined sampling locations to assess soil inhomogeneity. The data collected from post-treatment sampling and analysis will be used in a geostatistical model to determine the likely distribution of contamination remaining in the soil and the statistical significance of the results.

A detailed economic analysis of this full-scale technology application will be performed utilizing monitoring data (i.e., water, chemical, and gas usage; waste generation; and maintenance needs). This data was collected by the developer with oversight by the SITE Program during the course of operation. This analysis will focus on the actual costs of the full-scale remediation as well as theoretical costs at another site.

Key findings from the demonstration, including complete analytical results and the economic analysis, will be published in an Innovative Technology Evaluation Report. This report will be used to evaluate the *in situ* SERP technology as an alternative for cleaning up similar sites across the country. Results will also be presented in a SITE Technology Capsule and a videotape.

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ELECTROKINETIC SOIL REMEDIATION- A PILOT SCALE STUDY

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INTRODUCTION

The demand to develop innovative and cost-effective in-situ remediation technologies in waste management stimulated the effort to employ conduction phenomena in soils under an electric field to remove chemical species from soils (1-15). This technique variably named as *electrokinetic remediation, electro-reclamation, electrokinetic soil processing, electro-chemical decontamination or electrochemical soil processing* uses low-level DC in the order of mA/cm^2 of cross sectional area between the electrodes or an electric potential difference in the order of a few volts per cm across electrodes placed in the ground in an open flow arrangement. The groundwater in the boreholes or an externally supplied fluid (processing fluid) is used as the conductive medium. Open flow arrangement at the electrodes allows ingress and egress of the processing fluid or the pore fluid into or out of the porous medium. The low-level DC results in physico-chemical and hydrological changes in the soil mass leading to species transport by coupled and uncoupled conduction phenomena in the porous media. Electrolysis reactions prevail at the electrodes. The species input into the system at the electrodes (either by the electrolysis reactions, or through the cycling processing fluid) and the species in the pore fluid will be transported across the porous media by conduction phenomena in soils under electric fields. This transport coupled with sorption, precipitation and dissolution reactions comprise the fundamental mechanisms affecting the electrokinetic remediation process. Extraction and removal are accomplished by electrodeposition, precipitation or ion exchange either at the electrodes or in an external extraction system placed in a unit cycling the processing fluid (16-18).

Electrokinetic remediation technology has recently taken significant strides. Geokinetics corporation of Netherlands has reported some field studies (12, 19) and Electrokinetics Inc. of Baton Rouge, USA has completed large-scale pilot studies, is conducting a field study expected to lead to a demonstration study under the SITE program. This paper presents a summary of the results of some of the pilot-scale studies conducted by Electrokinetics Inc. in collaboration with Louisiana State University. The main objectives of the pilot-scale studies were to assess the efficiency of the technique when bench-scale testing conditions are up-scaled to size and geometry more representative of field conditions and to evaluate the techgnique by conducting a well-documented large-scale study with proper quality

assurance. A second objective was to use the results of these studies to compare with the results of the numerical implementation of a theoretical model developed at Louisiana State University.

METHODOLOGY

Two pilot-scale tests are conducted using kaolinite spiked with lead at initial concentrations of 850 mg/kg, 1,500 mg/kg and another with using fine sand and kaolinite mixture spiked with lead at 5,000 mg/kg. Figure 1 presents a schematic diagram of the container used for the pilot-scale study . The dimensions of the container are 91 cm by 182 cm in width and length and 91 cm in depth. These dimensions are selected in an attempt to minimize boundary effects, simulate one-dimensional transport conditions and represent an intermediate electrode spacing between bench-scale and full-scale field implementation. Inert graphite rods are used both for the anode and the cathode. Constant current conditions are employed in testing . Tensiometers are installed across the electrodes to measure development of pore pressures. Voltage probes allowed development of electrical potential gradients. Specimens are taken across the electrodes in time to record the changing chemistry.

The kaolinite used had lead adsorption capacity of about 1,100 mg/kg. Lead nitrate salt is used as the source of lead. Tap water is used both as the catholyte and the anolyte. Positively charged species prematurely precipitate close to the cathode when the chemistry of the electrolyte at the electrodes is not altered or controlled (unenhanced electrokinetic remediation) . Acar and Alshawabkeh (2) discuss the need for enhancement and propose different enhancement techniques which prevent the encountered precipitation. An enhancement technique is not used in the pilot-scale studies reported herein since the specific tests also served in evaluation of a theoretical model of electrokinetic remediation. Other details of the testing are presented by Alshawabkeh (20). Enhancement techniques and enhanced pilot-scale studies using a soil from a lead contaminated site are ongoing at Electrokinetics Inc.

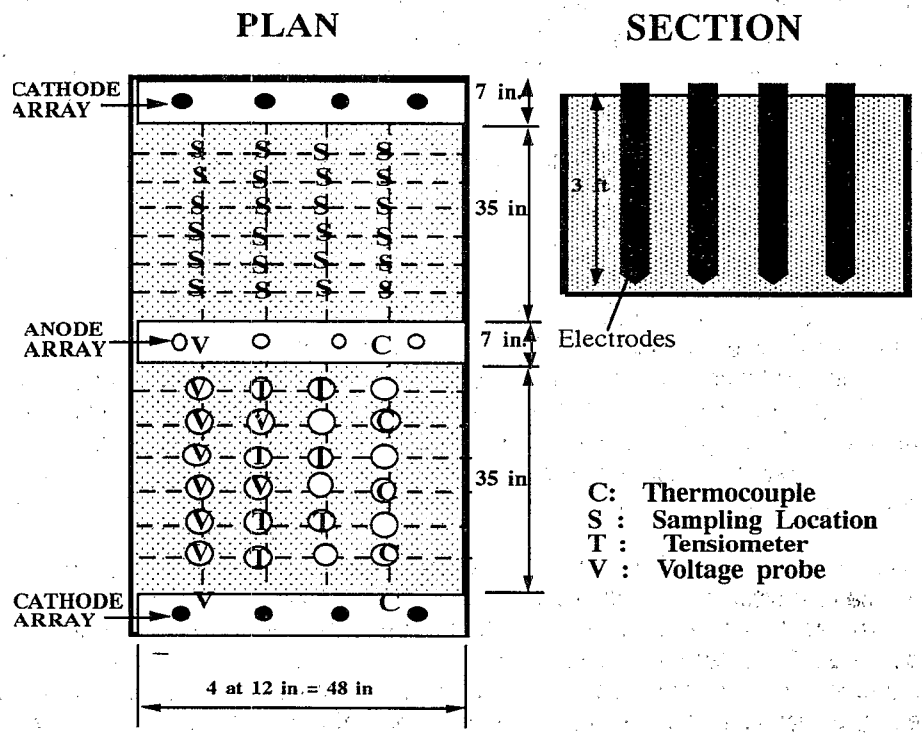

Figure 1. A Schematic Diagram of the Pilot-scale Test Set-up and the Data Collection Locations

RESULTS

Thedetailed results of this study are presented by Alshawabkeh (20). Some findings are herein presented. Figure 2 presents a contour diagram of lead distribution across the electrodes after 2952 hours of testing at 130 $\mu A/cm^2$. An apparent electrical gradient of 2 V/cm was attained. The energy expenditure in this test was close to 700 kWh/m^3 of soil processed. The power expenditure was almost constant at 270 W/m^3 after an initially lower power expenditure period. The apparent electrical conductivity was about 70 $\mu S/cm$. The precipitation close to the cathode is confined to the last10 cm of length. The pH outside the zone of precipitation increased from about 2 to 4. The pH within the zone of precipitation was mostly 5 and the it increased to 10 to 11 in the catholyte. There was not any electroosmotic flow in this test. Excluding the zone of precipitation, lead was remediated by 98 %. Remediation at discretepoints outside the last 10 cm ranged between 90 % to 98 %. Final lead concentrations across the soil ranged between 30 mg/kg to 70 mg/kg with some points as high as 150 mg/kg. 70 % of the lead was in the last 2 cm and 15 % precipitated on the filter at the cathode compartment.

The acid front generated at the anode flushes across the soil mass and meets with the base front generated at the cathode at a zone close to the cathode compartment. The lead adsorbed on the soil and in the pore fluid moves across the soil mass by ionic migration as there is no electroosmotic flow. At the zone where the low pH front meets the high pH front, lead precipitates. Most of the electrical resistance across the electrodes is due to the low conductivity developed within this zone due to the merging pH fronts. Power expenditure is mostly due to resistance offered by this zone. Enhancement by depolarization of the cathode reaction prevents development of this zone and hence leads to even lower

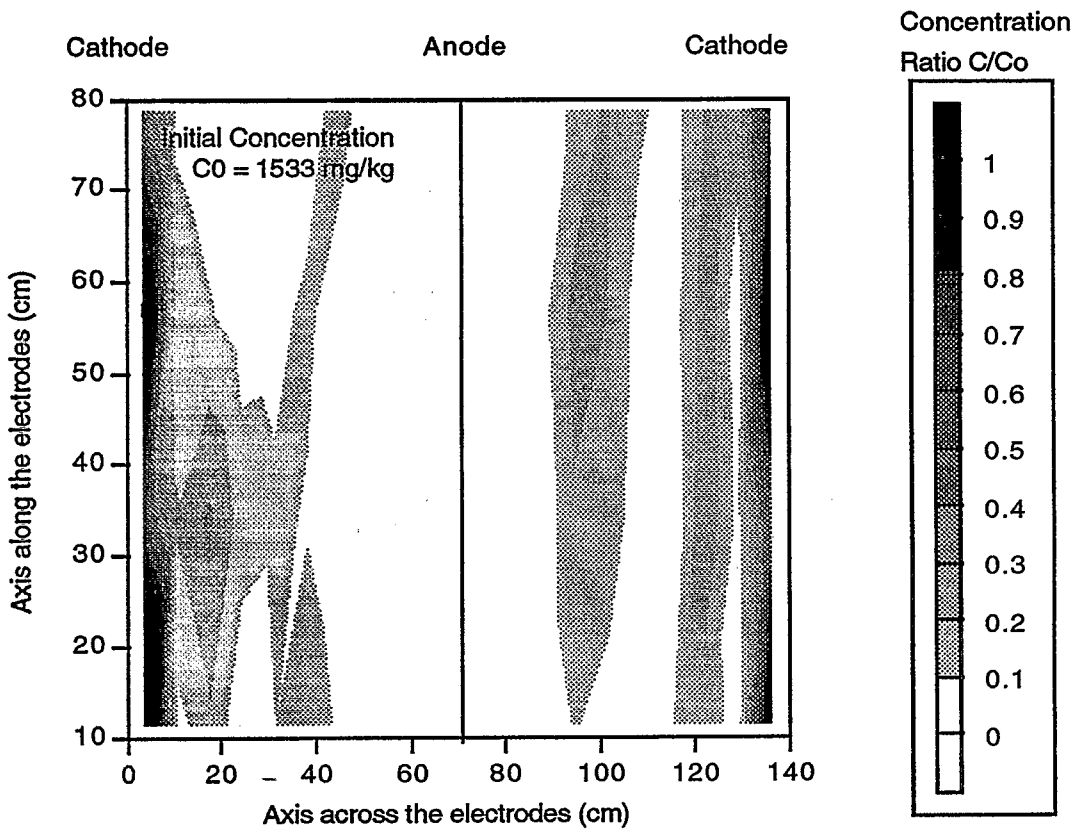

Figure 2. Contour diagram of lead removal across the electrodes in unenhaced electrokinetic remediation of lead spiked Georgia kaolinite

power expenditures (4). However, the acid used in depolarization is then an additional cost to the process.

CONCLUSIONS

These studies demonstrate that the efficiency achieved in bench-scale studies in electrokinetic remediation is attainable at the pilot-scale. It is demonstrated that lead is efficiently removed by 90 % to 98 % across the electrodes even when there is no electroosmotic flow across the medium. In most contaminated soils and site conditions, ionic migration will be the predominant transport mechanism in electrokinetic remediation (2). As in the unenhanced bench-scale tests, precipitation occurred very close to the cathode with the increase in pH. Most of the energy expenditure is due to formation of this low resistivity zone.

These results together with ongoing pilot-scale studies and studies investigating different enhancement techniques demonstrate that the efficiency and cost-effectiveness of the technique in remediation depend upon the complexity of contamination encountered together with employment of an effective enhancement technique. A comprehensive chemical speciation/characterization and site specific bench-scale and pilot-scale treatability studies may be necessary in field implementation of the technique at a specific site.

REFERENCES

1. Acar, Y. B. Electrokinetic Soil Processing; A Review of the State of the Art . In: Proceedings of the ASCE Grouting Conference, ASCE Special Publication No. 30, v. 2, pp. 1420-1432, 1992.

2. Acar, Y.B., Alshawabkeh, A. Principles of Electrokinetic Remediation . Environmental Science and Technology, vol. 27, n. 13, pp. 2638-December 1993.

3. Acar, Y. B., Alshawabkeh, A., Gale, R. J. Fundamentals of Extracting Species from Soils by Electrokinetics. Waste Management , Pergamon Press, New York, 12 (3): 1410-1421 , 1993.

4. Acar, Y.B., Puppala, S., Marks, R., Gale R.J., Bricka, M. *An Investigation of Selected Enhancement Techniques in Electrokinetic Remediation,* Report presented to US Army Waterways Experiment Station, Electrokinetics Inc., Baton Rouge, Louisiana, 1993, 160 p.

5. Acar, Y.B., Gale, R.J., Ugaz, A., Marks, R., Feasibility of Removing Uranyl, Thorium and Radium from Kaolinite. In: Proceedings of 19th Annual RREL Hazardous Waste Research Symposium, EPA/600/R-93/040, 161.

6. Acar, Y. B., Li, H., Gale R. J. Phenol Removal from Kaolinite by Electrokinetics, Journal of Geotechnical Engineering, v.118, No. 11, pp. 1837-1852, 1992.

7. Acar, Y. B., Gale, R. J., Ugaz, A., Puppala, S., Leonard, C. Feasibility of Removing Uranium, Thorium and Radium from Kaolinite by Electrochemical Soil Processing. EK-BR-009-0292, Final Report-Phase I of EK-EPA Cooperative Agreement CR816828-01-0, Electrokinetics Inc., Baton Rouge, Louisiana, 1992, 243 p.

8. Acar, Y. B., Gale R. J., Leonard, C. QAPP-Phase I; Project EKSITE. Quality Assurance Project Plan

submitted to Office of Research and Development, RREL, Electrokinetics Inc. , Baton Rouge, Louisiana, EK-BR-002-0390, 1990, 126 p.

9. Acar, Y. B., Gale, R. J., and Putnam, G. Electrochemical Processing of Soils: Theory of pH Gradient Development by Diffusion and Linear Convection. Journal of Environmental Science and Health, A25 (6): 687-714, 1990.

10. Alshawabkeh, A., Acar, Y.B. Removal of Contaminants from Soils by Electrokinetics: A Theoretical Treatise, Journal of Environmental Science and Health v.27, 7, pp.1835-1861, 1992.

11. Hamed, J., Acar, Y. B., and Gale, R. J. Pb(II) Removal from Kaolinite Using Electrokinetics, Journal of Geotechnical Engineering, ASCE, Vol. 112, pp.241-271, 1991.

12. Lageman, R.; Wieberen, P.; Seffinga, G. Electro-Reclamation:Theory and Practice. Chemistry and Industry, Society of Chemical Industry, London, pp. 585-590, 1989.

13. Pamukcu, S. ; Wittle, J. K. Electrokinetic Removal of Selected Heavy Metals from Soil. Environmental Progress, **11** (3), pp. 241-250, 1992.

14. Probstein, R.F.; Hicks, R. E. Removal of Contaminants from Soils by Electric Fields. Science, 260, pp. 498-504, 1993.

15. Runnells, D.D.; Wahli, C. Insitu Electromigration as a Method for removing Sulfate, Metals and Other Contaminants from Ground Water. Ground Water Monitoring Review and Remediation., **11** (3), 121, 1993.

16. Wieberen, Pool . A Process for electroreclamation of soil material, an electric current system for application of the process and an electrode housing for use in the electric current system. EEC Patent No: EP 0 312 174 A1, April 19, 1989.

17. Probstein, R.F., Brookline, P.C.R., Shapiro, A.P. Electroosmosis Techniques for removing materials from soils. US Patent No. 5,074,986, Dec. 24,1991.

18. Acar, Y. B., and Gale, R. J.. Electrochemical Decontamination of Soils and Slurries. US Patent No. 5,137,608, Commissioner of Patents and Trademarks, Washington, D.C., August 11, 1992.

19. Lageman, R. Electroreclamation-Applications in the Netherlands. Environmental Science and Technology, v. 27, pp. 13, pp. 2648-2650.

20. Alshawabkeh, A.N. Theoretical and Experimental Modeling of Removing Contaminants from Soils by Electrokinetics. PhD Dissertation, Louisiana State University (1994).

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COGNIS TERRAMET™ LEAD EXTRACTION PROCESS

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INTRODUCTION

The COGNIS TerraMet™ lead extraction process leaches and recovers heavy metals, and specifically lead, from contaminated soil with one of several proprietary aqueous leaching solutions. The leachant is specifically matched with the substrate and level and type of lead contaminants. In this way the system can deal with most types of lead contamination including lead salts, oxides and metallic lead. Complete leaching of lead is difficult considering the nature of the problem: the variability, inhomogeneity, the presence of lead in both metallic and ionic form, and the natural binding properties of soils containing clays, iron and manganese oxides and humus. The leaching conditions studied in this project were chosen to be physically, economically, and ecologically acceptable, and the leachant had to allow recovery of the leached metals so that the leachant could be reused directly without pH adjustments. The metal recovery process had to deliver the metals in a compact form which would be easily recycled and reused.

The bench-scale results from an EPA SITE Emerging Technology Project are described here. In addition, a brief summary of results from a full-scale implementation of the TerraMet technology at the Twin Cities Army Ammunition Plant (TCAAP), New Brighton MN will be shown.

METHODOLOGY

The leaching-metal recovery concept is illustrated in Figure 1. The contaminated soil is contacted with a leaching agent which dissolves a portion of the lead. The lead is removed from the lead-rich leachant in a metal recovery stage. The lead-depleted leachant then contacts the soil a second time. The process is repeated until the lead concentration in the soil is acceptably low. This approach completely recycles the leaching agent. Thus, the metal bearing leachant never leaves the process, no liquid waste streams are generated, and metal recovery can be tailored to the site.

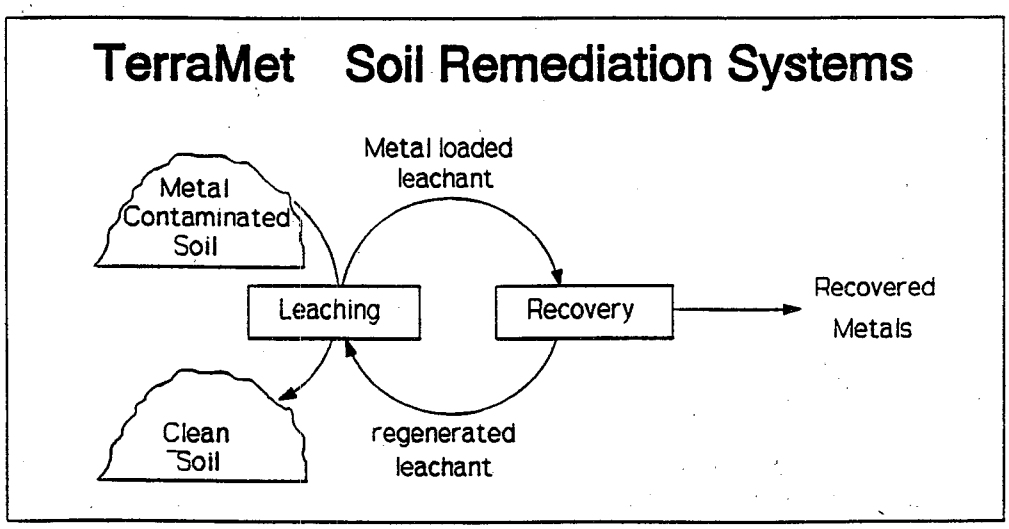

Figure 1. Lead Leaching - Recovery Concept

The preferred recovery process for lead is direct reduction of the dissolved ionic lead to lead metal. Other metal recovery options have been tested, and the most appropriate recovery process for a specific site depends on the leachant required and the amount and type of metals present.

The goal of the SITE Emerging Technology project was to test the leaching-lead recovery concept at the bench-scale, study the efficacy of various leachants, and verify that the lead recovery stage worked. Figure 2 illustrates the steps involved. This bench-scale testing was done with 2 g of soil. This allowed a single soil sample to be weighed, leached multiple times, and the entire leached soil sample to be digested after leaching without having to transfer soil from the leaching vessel. The lead contained in the original contaminated soil sample is then equal to the lead contained in the *n*-leachant solutions plus the lead in the treated soil (measured by EPA acid digestion). After verification of the concept on a particular soil, the leaching process was scaled up and converted to a continuous leaching process on a 500 g soil scale. The continuous bench-scale process proved that lead could be removed from the lead-rich leachant and that the lead-depleted leachant could be recycled for continued leaching of the soil.

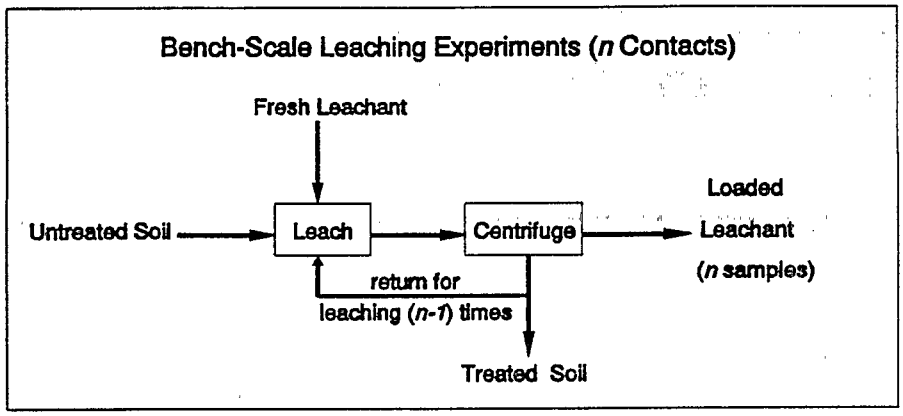

Figure 2. Process Flow Diagram for Bench-Scale Testing

RESULTS

Table 1 demonstrates bench-scale leaching of soil contaminated with lead as a result of a leaking underground storage tank. The soil was excavated from around the leaking fuel tank and therefore contains mineralized inorganic lead residues from the decomposition of tetraethyl lead in the released gasoline. The initial contamination concentration is relatively mild (250 - 300 ppm), but high enough to fail the TCLP test. Consecutive leaching contacts resulted in residual lead concentrations in the soil of 20 - 25 ppm.

Table 1.
LEACHING OF SOIL FROM LEAKING UNDERGROUND STORAGE TANK

Cumulative % Pb Leached						Initial	Final
Leaching Contact #						[Pb]	[Pb]
1	2	3	4	5	6	(ppm)	(ppm)
63	80	85	87	89	90	256.5	25.5
50	66	89	91	92	93	311.5	22.5

Table 2 contains results from leaching of sandblasting waste containing leaded paint chips and dust. This material was contaminated in the range of 4,000 - 4,500 ppm lead initially, and with six consecutive leaching contacts it proved possible to remove all but approximately 200 - 250 ppm lead. This residual concentration was well below the regulatory goal of <500 ppm lead.

Table 2.
LEACHING OF LEADED PAINT SANDBLASTING WASTE

Cumulative % Pb Leached						Initial	Final
Leaching Contact #						[Pb]	[Pb]
1	2	3	4	5	6	(ppm)	(ppm)
73	87	91	93	94	95	4329	237
75	88	92	94	95	96	4596	206

Soil from an ammunition test burning area (TCAAP) was also studied. At this site both metallic lead fragments as well as ionic lead was found. Because of the high density of lead relative to most soil constituents, the coupling of soil washing with density separation was a logical pretreatment to leaching. Soil was first size classified, then density separated using standard mineral processing equipment to remove heavy lead fragments. Tables 3 and 4 show the results on leaching of the fines and density pretreated sand fraction. Leaching the fines was very effective and gave residual lead concentrations of <20 ppm with leachants #2 or #3. The results on the sand were equally satisfactory. Residual lead concentration of < 70 ppm was also achieved with leachants #2 or #3.

Table 3.
LEACHING OF TCAAP -200 MESH FINES WITH VARIOUS LEACHANTS

	Cumulative % Pb Leached					Initial	Final
	Leaching Contact #					[Pb]	[Pb]
Leachant	1	2	3	4	5	(ppm)	(ppm)
1	53	71	79	83	86	616	87
1	50	68	76	81	84	587	95
2	59	90	96	97	97	575	16
2	64	92	97	98	98	608	11
3	80	94	97	98	98	640	12
3	81	96	98	99	99	638	7

Table 4.
LEACHING OF TCAAP DENSITY PRETREATED 8 to 200 MESH SAND WITH VARIOUS LEACHANTS

	Cumulative % Pb Leached					Initial	Final
	Leaching Contact #					[Pb]	[Pb]
Leachant	1	2	3	4	5	(ppm)	(ppm)
1	66	80	84	87	88	255	31
1	69	82	86	89	90	205	21
2	49	71	81	85	88	585	69
2	75	87	90	92	93	190	14
3	71	82	86	89	90	221	21
3	80	92	95	96	97	223	<7

After the small bench-scale experiments proved the success of the multiple leaching concept, additional larger scale continuous leaching experiments verified the leaching results obtained earlier. The continuous-scale apparatus more closely approximates full-scale treatment. It employs an agitated leaching vessel from which a soil slurry is pumped into a clarifier. The clarifier separates the slurry into a clarified feed at the overflow and a thickened slurry at the underflow. The underflow is continuously returned to the leaching vessel. The overflow is pumped into the metal recovery unit where the lead is

removed from the leachant and the lead recovered as solid lead powder. The lead-depleted leachant is then returned to the leaching vessel for continued leaching. After leaching is complete, the soil-leachant slurry is dewatered and neutralized. Thus, the entire leaching, clarification, and metal recovery process operates continuously on the batch of soil in the leaching vessel. Table 5 illustrates typical data on ammunition plant soil. Routinely < 100 ppm residual lead and TCLP passage was observed. The lead concentrations shown under the influent and effluent columns are the concentrations of lead in the leachant entering and exiting the metal recovery unit.

Table 5.
CONTINUOUS-SCALE LEACHING EXPERIMENT TCAAP SOIL (DENSITY PRETREATED)

Matrix	Lead Concentration (μg/g)	
	Pre-Leaching	Leached
Soil (Avg)	250 - 350	31.1
Replicate 1		32.6
Replicate 2		28.2
Replicate 3		33.2
Leachate	Influent (μg/mL)	Effluent (μg/mL)
Sample 1	15.4	2.5
Sample 2	10.6	2.1
Sample 3	4.6	1.3
Sample 4	2.5	0.7
Sample 5	1.4	<0.5
Sample 6	0.9	<0.5
Sample 7	0.5	<0.5

CONCLUSIONS

The COGNIS TerraMet™ lead extraction process has been successfully proven at the bench-scale on several sites: a leaking underground leaded gasoline tank, leaded paint-sandblast waste, and on the Twin Cities Army Ammunition Plant (TCAAP) soil.

The TCAAP results led to the construction of a full-scale lead remediation plant. The plant utilizes continuous, multiple leaching contacts and the continuous metal recovery concept proven in the SITE Emerging Technology project. The treatment train at TCAAP also uses a Bescorp soil washing plant which physically pretreats the soil to remove the dense particulate lead fragments and separates the soil into three fractions: a clean gravel fraction and contaminated sand and fines fractions. The sand and fines are leached in two parallel streams in the TerraMet plant. The combined plant utilizes full recycle of all aqueous solutions and 1,600 tons of lead-contaminated soil were processed through the full-scale system at TCAAP in mid-September through October, 1993.

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ACID EXTRACTION TREATMENT SYSTEM (AETS) FOR TREATMENT OF METAL CONTAMINATED SOILS

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INTRODUCTION

Through a Cooperative Agreement with the U.S. Environmental Protection Agency's (EPA) Risk Reduction Engineering Laboratory, the Center for Hazardous Materials Research (CHMR) developed the Acid Extraction Treatment System. The project was conducted with support from Interbeton bv and The Netherlands Organization for Applied Scientific Research (TNO). AETS is intended to reduce the concentrations and/or leachability of heavy metals in contaminated soils to render the soils suitable to be returned to the site from which they originated. Additional applications may include treatment of contaminated sediments, sludge, and other heavy metal-containing solids.

The objective of the project was to determine the effectiveness and commercial viability of the AETS process in reducing the concentrations and leachability of heavy metals in soils to acceptable levels. This abstract briefly describes the activities conducted during the project, the experiments performed, and the results.

A pilot scale system was designed, constructed, and used to test different soils. Five soils were tested, including EPA Synthetic Soil Matrix (SSM), and soils from four Superfund sites (NL Industries in Pedricktown, NJ; King of Prussia site in Winslow Township, NJ; Silver Bow Creek site in Butte, MT; and Palmerton Zinc site in Palmerton, PA). These soils contained elevated concentrations of arsenic, cadmium, chromium, copper, lead, nickel, and zinc.

Many experiments were conducted with this pilot-scale system, and the data obtained from these experiments were used to produce several cost estimates for processing the soils through a full-scale plant. These cost estimates are based on several different parameters, such as size of site, levels of contaminants, and residence time.

METHODOLOGY

Process Description

A simplified block flow diagram of the AETS process is shown in Figure 1. Full-scale units are anticipated to be able to process between 10 and 30 tons per hour. The first step in the full-scale AETS process is screening to remove coarse solids. These solids, typically greater than 4 millimeter (mm) in size, are anticipated to be relatively clean, requiring at most a simple rinse with water or detergent to remove smaller attached particles.

After coarse particle removal, the remaining soil is scrubbed in an attrition scrubber to physically remove the metals and break up agglomerations. Then it is contacted with hydrochloric acid (HCl) in the extraction unit. The residence time in the unit may vary depending on the soil type, contaminants, and contaminant concentrations, but is anticipated to range between 10 and 40 minutes. The soil and extractant mixture is continuously pumped out of the mixing tank, and the soil and extractant are separated using hydrocyclones. The solids are piped to the rinse system, while the cyclone overflow (extractant) is treated using a proprietary technology which removes the metals from the liquid and regenerates the acid.

The soils are rinsed with water to remove entrained acid and metals. The metals are removed from the rinsate using the same technology that regenerates the acid. After rinsing, the soil is dewatered using hydrocyclones and (if required) dewatering screens. In the final step, the soils are mixed with lime and fertilizer to neutralize any residual acid and return the soil to natural conditions.

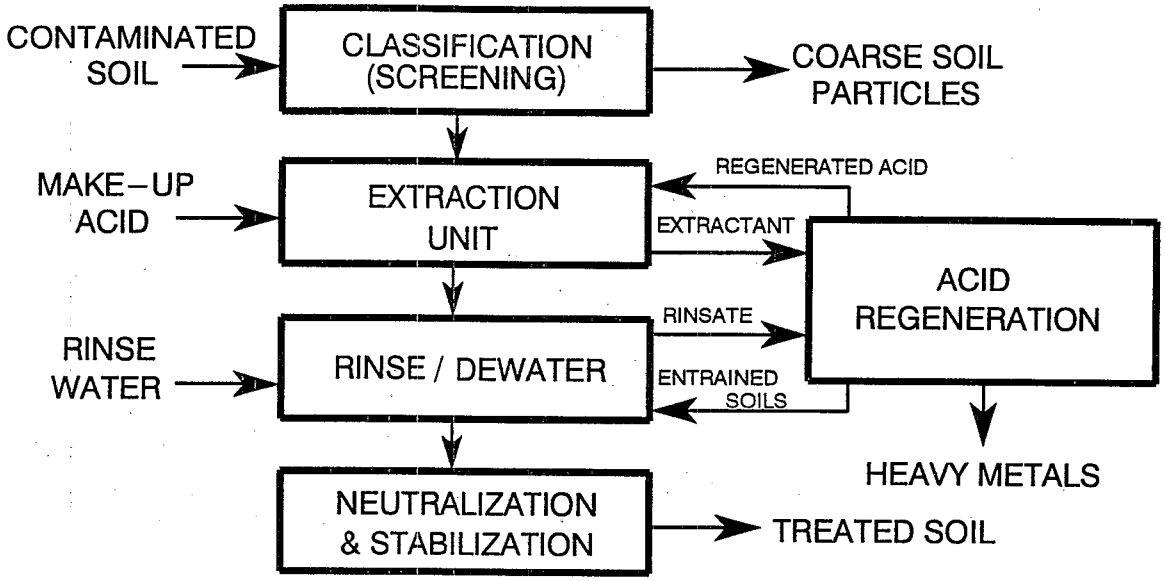

FIGURE 1. AETS BLOCK FLOW DIAGRAM.

Experimental Procedure

The pilot-scale AETS unit was constructed and tested in CHMR's Technology Development Laboratory. This system is capable of processing between 20 and 100 kilograms (kg) of soil per hour. The soils were initially characterized for total metals and Toxicity Characteristic Leaching Procedure (TCLP) metals content. The soils were screened to remove the +8 mesh fraction on a mechanical shaker prior to being placed in the lab-scale attrition scrubber, where the soil was slurried with water (or regenerated hydrochloric acid from previous experiments) prior to entering the extraction vessel.

Next, the soil was contacted with the hydrochloric acid for residence times between 10 and 40 minutes in the extraction tank. The pH of the mixture was maintained between 1.8 and 2.2. During extraction, the solids were separated using two hydrocyclones, and returned to the extraction tank. The extractant was pumped to the acid regeneration system, and then returned to the extraction tank.

At the end of the experiment, the soil was dewatered using two cyclones and a mechanical shaker with a 200 mesh screen to separate the solids and the extractant. The extractant was then regenerated to be used as the acid in the next experiment, and the solids were prepared for the rinsing step.

The solids were rinsed in water to remove any residual acid. The metals were removed from the rinse water using a separate regeneration system than the one used during the extraction. The clean solids and all liquids were then analyzed for total and TCLP metals to form a material balance. The extractant and rinse water were ready for use in the next experiment, so no waste streams were generated during the experiments.

Experimental Soils

This section gives a brief discussion of the soils used during the laboratory- and pilot-scale investigations. These soils included the EPA's SSM, and soils from: NL Industries Site in Pedricktown, NJ, Silver Bow Creek Site in Butte, MT, King of Prussia Site in Winslow, NJ, and the Palmerton Zinc Site in Palmerton, PA.

The SSM is produced by the EPA specifically for use in research and development of emerging or innovative technologies. The soil is a mixture of clay, silt, sand, gravel, and topsoil that is blended together to form the soil matrix. Organic and inorganic contaminants are added based on typical hazardous materials at Superfund sites. This soil contained approximately 10,000 milligrams per kilogram (mg/kg) total lead and 27 milligrams per liter (mg/L) of TCLP lead.

The NL Industries site, located in Pedricktown, NJ, was an integrated battery breaking and lead smelting facility. The soil is contaminated with copper, lead, and zinc, but was chosen for this project due to the high levels of lead. The total and TCLP lead values were 29,000 mg/kg and 520 mg/L, respectively.

The King of Prussia site was used to neutralize acid streams from an adjacent site. The soil is contaminated with chromium, copper, and nickel, and it is not hazardous by RCRA standards. The site was placed on the National Priorities List (NPL) because of high levels of chromium. The soil contains approximately 1,200 mg/kg of total chromium.

The Silver Bow Creek Site contains a very sandy soil, with very little clay. The soil is contaminated with copper and zinc, with the total metals of 120 mg/kg and 1,250 mg/kg, respectively. The TCLP values were 1.5 mg/L for copper, and 5.0 mg/L for zinc. The Butte soil is not considered hazardous soil.

The Palmerton site is an old zinc smelting facility. Only one experimental extraction was conducted on this material, due to a lack of soil. This soil was chosen because of its high levels of zinc, and because it contained lead, cadmium, and copper. The Palmerton soil contained 1,000 mg/kg total lead, and 10,000 mg/kg total zinc.

RESULTS

Experimental Results

Table 4 qualitatively summarizes the soil treatability for the soils and metals tested. For soils with a high amount of clay, that clay fraction was treated and analyzed separately with the AETS system. The table reports the results as if all fractions were remixed at the conclusion of the experiment. The results show that AETS treated virtually all the soils tested to reduce both the total and TCLP metals concentrations to below currently regulated concentrations. The only exceptions were cadmium, which consistently failed the TCLP for SSM soil, and lead, which failed both the TCLP and total metals requirements for SSM soils.

TABLE 1. QUALITATIVE RESULTS OF EXTRACTIONS

Metal	SSM	Butte	King of Prussia	Pedricktown	Palmerton
As	*, T, L	*, T, L			
Cd	*, T				*, T, L
Cr	*, T, L		***, T, L**[†]	*, T, L	
Cu	***, T, L**	*, T, L	*, T, L		*, T, L
Ni	*, T, L		*, T, L		
Pb	*	*, T, L		***, T, L**	*, T, L
Zn	***, T, L**	*, T, L		*, T, L	*, T, L

* - Metal is present in the soil
T - Successful treatment for total metals
L - Reduction in leachability to below standards
[†]Bold and large fonts indicate high initial metals content (at least double regulatory standards)

Table 2 shows typical results obtained from the lead contaminated soil from the NL Industries Superfund site in Pedricktown, NJ. The table shows over 90% reductions in total metals concentrations, and a 99% reduction in TCLP. Further work indicated that the TCLP and total lead

in the soil could be reduced to below 5 mg/L and 1000 mg/kg, respectively. These are the EPA recommended levels for remediation of lead in soil. The experimental work was completed during January 1993, and the final report has recently been issued.

TABLE 2. NL INDUSTRIES SOIL

	Total Metals (mg/kg)			TCLP Metals (mg/L)		
Metal	Initial	Final	% Removal	Initial	Final	% Removal
Pb	29,200	1,310	95.5	520	5.1	99.0

Economic Analysis

CHMR constructed an economic model of a full-scale AETS system based on the results of the pilot-scale experiments. This economic model used such parameters such as: typical removal efficiencies, metal concentrations in the soil, extraction residence time, site size, etc. Some cost estimates for various situations are presented in Table 3 below. CHMR has estimated that a full-scale AETS processing unit could be built to process soil at between $80 and 240 per cubic yard (yd^3).

TABLE 3. AETS COST SUMMARIES UNDER VARIOUS CONDITIONS

Capital and Operating Costs ($/$yd^3$)	Feed Rate (yd^3/hr)	Extraction Residence Time (min)	% Fines (<50 μm)	Metals Conc. (mg/kg)	Site Size (1000 yd^3)
77	22.9	24	15	5,000	114.7
96	15.3	24	15	15,000	76.5
138	15.3	36	30	15,000	45.9
118	15.3	24	15	15,000	61.2
122	11.5	24	15	5,000	45.9
193	11.5	36	30	15,000	22.9
168	11.5	36	15	5,000	22.9
241	7.6	36	30	15,000	15.3

The following notes apply to this table:

1. The plant is operating for only 1 eight hour shift per day.
2. No metal recovery value is assumed. All metal sludge is disposed.

This table includes costs for mobilization, pilot plants, excavation, replacing soil, and reseeding the ground as well as the actual soil treatment. Thus, the costs represent *total costs* of treatment using the AETS. Note that the table conservatively assumes that the capital costs of the AETS are amortized over only 1 site, and that the plant operates only one eight hour shift per day. Finally, the economic model assumes that the metal sludge is stabilized and disposed, and not reclaimed. The metals at many sites may be reclaimable. Relaxing all of these conservative assumptions will reduce the estimated treatment costs by 20 to 30%.

CONCLUSIONS

The conclusions derived from the study are summarized below:

- AETS is capable of treating a wide range of soils, containing a wide range of heavy metals to *reduce the TCLP below the RCRA limit and to reduce the total metals concentrations below the California-mandated total metals limitations.*

- In most cases, AETS is capable of treating the *entire* soil, with no separate stabilization and disposal for fines or clay particles. For most of the soils tested, AETS can do this to the required TCLP and total limits. The only exception to this among the soils tested was with the SSM, which may require separate stabilization and disposal of 20% of the soil because of lead. This soil was successfully treated for other metals, including arsenic, chromium, copper, nickel and zinc.

- Costs for treatment, under conservative process conditions, range between $80 and 240 per cubic yard of soil, depending on the site size, soil types and contaminant concentrations, as well as several other parameters.

ACKNOWLEDGEMENTS

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TREATMENT OF ORGANIC WASTES IN AQUEOUS MATRICES BY X-RAY

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ABSTRACT

Titan/Pulse Science Inc. (PSI) is presently funded jointly by the U.S. Environmental Protection Agency (US EPA) and the Department of Energy (DOE)under the SITE Emerging Technology program to develop and demonstrate the x-ray (Bremsstrahlung radiation) processing concept for the treatment of solid and liquid wastes contaminated with volatile (VOCs) and semi-volatile (SVOCs) organic compounds.

X-ray treatment technology is based on the in-depth deposition of ionizing radiation. Collisions of energetic photons (x-rays) within the contaminated waste generate a shower of lower energy secondary electrons which ionize and excite the atomic electrons, break up the complex contaminant molecules, and form radicals that react with the VOC or SVOC contaminant to form compounds such as water, carbon dioxide and oxygen.

A 1.2 MeV, 800 A, 55 nsec electron beam from a linear induction accelerator (LIA) impacts a high-Z tantalum target which converts the electron pulse into x-rays. The LIA is pulsed at the rate of one pulse per second giving a dose rate at the sample of $\leq$ 5 rads per second.

Preliminary results of the compounds in aqueous matrices evaluated included contaminants in actual Superfund well water samples as well as neat samples of trichloroethylene (TCE), tetrachloroethylene (PCE), benzene, toluene, and carbon tetrachloride in deionized water. The concentration ranged from 100 to 64,000 ppb.

Irradiated contaminants with concentrations ranging from 100-4000 ppb were decomposed at x-ray doses of less than 200 kilorads (krads). Most of the other irradiated contaminants decomposed at dose levels less than 200 krads with no residual by-products detected. However, a limited number of experiments conducted for TCE at higher concentrations (64,000 ppb) showed the presence of hazardous by-products which mineralized as the x-ray dose was increased, however, it is not clear whether toxic residuals are formed and/or completely mineralized and, if so how much? This is still under investigation. This paper will present only preliminary results obtained from the study.

INTRODUCTION

Electron beam processing has been established as highly effective in the destruction of organic compounds in the removal of chemicals SO_x and NO_x, the chemicals that cause acid rain, from power plant and incinerator stack gases; (Ref. 1) disinfection of sewage and plastics processing waste. (Ref. 1 - 10) High energy photons, gamma-rays are routinely used to sterilize medical supplies. (Ref. 12) It has been observed that all forms of ionizing radiation (electron beam, gamma-rays and x-rays) have

approximately the same chemical effects for a given dose. Electron beams with energies in the range of 1-5 MeV have been generated using conventional accelerators. For those energies the range of electron penetration is limited to 0.3-2 cm for a material with a density of 1 g/cm^3. The use electron beams would require that the material will in the form of a thin stream or slab which may require substantial material preprocessing and handling.

Gamma-rays, from radioactive cobalt offers greater penetration depths, however, the inability to turn off the radiation from the source presents an acceptable health hazard. X-rays produced when high energy electrons are stopped offer the same advantages as gamma-rays, penetrating more than five times further than electrons for the same electron beam source while providing the safety of an electron beam source which can be shut off when not in use. It is expected that a large number of organic wastes can be decomposed at an x-ray dose of ≤ 1 megarad (Mrad) or 10 joules/gram.

A high throughput x-ray treatment system requires the availability of a high average power electron accelerator capable of generating beams with energies of 5-7 mev. The upper limit on energy is a compromise between increased x-ray conversion efficiency at higher energies and the requirement that the energy be chosen small enough to avoid activation. (Ref. 1)

The U. S. EPA and the DOE under the Superfund Emerging Technology Program have entered into a cooperative agreement with Titan/Pulse Science Inc. (PSI) to evaluate the x-ray treatment process for the remediation of solid and liquid wastes contaminated with volatile (VOCs) and semi-volatile (SVOCs) organic compounds. The overall objective of the project is to demonstrate and develop the X-ray treatment concept for the destruction of organic contaminants in soil and water. The specific objectives are:

1) To demonstrate in pilot scale experiments the efficacy of x-ray treatment for solid and liquid waste contaminated with volatile organic compounds (VOCs) and semi-volatile compounds (SVOCs).

2) To determine the x-ray doses required to reduce organic contamination to acceptable levels, and

3) Develop the conceptual design for a high-throughput x-ray treatment system.

The linear induction accelerator (LIA) was first modified to include a high-Z x-ray target to convert the electron beam pulses into pulses of x-rays. Experiments to determine the x-ray doses needed for complete mineralization were begun during the later part of the first year of the program. During the last portion of the program, much higher concentrations of VOC/SVOC contaminated aqueous solutions will be irradiated with x-rays to investigate hazardous by-product formation and subsequent concentration levels of the by-products as the dose is increased.

METHODOLOGY

The proposed technology is based on the fact that as x-rays, gamma rays, and energetic electrons penetrate gases, liquids and solids they deposit energy primarily through ionizing collisions. These collisions generate energetic secondary electrons within the material which are effective in breaking up complex molecules and in forming chemically active radicals which will react with the contaminant materials.

The physical mechanism by which VOC and SVOC contaminants are removed is primarily dependent on the substrate. For example, in oxygenated water the primary reactant is the hydroxyl radical. This kinetic mechanism is also expected to play an important role in nonaqueous matrices, because of the

presence of moisture in contaminated soil, sludge and sediments.

In the presence of water the following reaction is known to occur:

$$H_2O \xrightarrow[\text{x-ray}]{} OH, e^-_{aq}, H_3O^+, H, H_2, H_2O_2$$

High throughput waste treatment applications for Superfund sites is made feasible by the use of high average power linear induction accelerator (LIA) for generating the 5-7 MeV electron beams required for maximizing the x-ray conversion efficiency while operating at an energy low enough to avoid producing radioactive by-products. (Ref. 1)

The operating principle of the LIA is analogous to that of an electrical transformer. (Ref. 1) The LIA at PSI has been modified to include an x-ray target which is used to convert electron beam pulses to pulses of x-rays. The target consists of a water cooled 2-mil titanium window, 5 mil tantalum foil, and a 0.2 inch thick carbon which acts as an electron stopper and debris shield. The 5-mil tantalum foil has been tested at up to 1000 A beam current. The accelerator is operating at a beam current of about 800 A at an electron beam energy of 1.2 MeV. The x-ray dose at the sample is measured using a radiochromic film. Scattering of electrons and x-rays in the converter serves to produce a broad x-ray beam which allows samples of 40 cm3 in volume to be irradiated simultaneously.

Samples sealed in 40 ml vials with teflon lined septums were placed in a rotating sample holder 10 cm from the tantalum foil and irradiated within a nitrogen filled irradiation chamber. The LIA is pulsed at the rate of one pulse per second to accumulate x-ray dose on the sample which is measured with radiochromic film. Since the average dose rate is approximately 5 rads per pulse or second, 200 pulses are required to deposit 1 Krad of energy in the sample. After irradiation the samples are analyzed by Gas chromatograph.

RESULTS AND CONCLUSION

Results of the 20 aqueous matrices are shown in Table 1. The first 15 were prepared using neat solutions of SVOC and VOCs in deionized water. The additional five matrices shown utilized well water drawn from either contaminated Superfund sites or working wells. The contamination level for the neat solutions varied from 13 ppb for cis-1,2-dichloroethene to 64,000 ppb for trichloroethylene indicate that the x-ray dosage needed to reduce the contaminants to <0.5 to 54 ppb is between 4 to 224 krad. As shown, compounds such as carbon tetrachloride require a much higher x-ray dose to destroy them than VOCs which react with the hydroxyl radical. In the presence of OH scavengers, such as carbonate ions, the x-ray dose required to destroy the VOC's increase somewhat. The spiked well water and Superfund water showed slightly higher x-ray doses when OH scavengers are present in the water. Both the spiked water well water and the two Superfund samples had high concentrations of carbonate and bicarbonate ions. This phenomena has been shown by Cooper et. al. (Ref 13) The carbonate and bicarbonate ions appear to act as OH scavengers. Benzene concentrations of 240 ppb and 262 ppb were irradiated in deionized water and well water. In deionized water 8.8 krads mineralized the benzene while 30.9 Krads was required for the mineralization of benzene in the well water. In addition the reaction rate depended on the diluting solution. The ethyl benzene and xylene samples of spiked well water also required slightly more x-ray dose to mineralize the contaminant.

A set of preliminary equations have been developed which allow the x-ray dose levels required to destroy VOCs in deionized water to be scaled to multiple VOC matrices and matrices containing OH scavengers, such as bicarbonates and carbonate ions. The scaling equations are based on the G-values calculated from the concentration-dose curve generated experimentally. The G-value is defined as the number of molecules of the contaminant which is formed or destroyed per 100 electron volts deposited

Table 1. Summary of Radiolysis Experiments: X-rays Treatment of VOC/SVOCs In Aqueous Matrices

Compound	Matrix	Initial Concentration (ppb)	Final Concentration (ppb)	X-ray Dose (kR)	Test Method
TCE	Deionized Water	64,000	<.5	180	8010
TCE		2100	<.5	20	8010
TCE		1000	<.5	10	8010
TCE		490	<.5	10	8010
PCE		230	3.6	4.2	8010
Chloroform		2000	4.4	178	8010
Methylene Chloride		270	3.1	145.9	8010
Trans 1,2 Dichloroethene		260	.78	10.6	8010
1,1,1 Trichloroethane		590	54	207.1	8010
Carbon tetrachloride		180	14	224	8010
Benzene		240	<.5	8.8	8020
Toluene		150	<.5	4.83	8020
Ethylbenzene		890	3.6	20.4	8020
Xylene		240	1.2	5.6	8020
Cis 1,2 Dichloroethene		13	<.5	10.6	8010
Benzene/carbon tetrachloride	FIU well water	262/400	<.5/196	39.9/93.8	FIU
Ethylbenzene/carbon tetrachloride	FIU well water	1000/430	<.5/70.9	33.2/185	FIU
D-xylene/carbon tetrachloride	FIU well water	221/430	<.5/85	20.5/171	FIU
Superfund Well Water Sample #1:					
TCE	SFWW1	3400	<.5	99.0	8240
PCE	SFWW1	500	<.5	99.0	8240
1,1-dichloroethane	SFWW1	21	1	145.4	8240
1,1,1 -trichloroethane	SFWW1	13	2.0	145.4	8240
Cis 1,2 dichloroethane	SFWW1	47	<.5	49.9	8240
Superfund Well Water Sample #2:					
TCE	SFWW2	5000	<1.0	291	8240
PCE	SFWW2	490	1.6	291	8240
Chloroform	SFWW2	250	81	291	8240
Carbon tetrachloride	SFWW2	14	4	291	8240
1,2 Dichloroethane	SFWW2	38	17	291	2840
1,1 Dichloroethane	SFWW2	11	6.8	291	8240
Freon	SFWW2	71	32	291	8240

SFWW1: Superfund well water #1 was a superfund sample which was comprised of the six contaminants shown.

SFWW2: Superfund well water #2 was a superfund sample comprised of the four contaminants shown.

energy. (Ref 14) The G-value is used for scaling the chemical reaction. Typical G-values reported range from 7-12. (Ref 14) Table 2 shows G-values derived from the experiments. The G- value has been found to be a measure of the efficiency of a reaction, the higher the G-value the more efficient is the reaction.

It was initially thought that any by-product formed during irradiation were also destroyed by the irradiation. The x-ray irradiation data for initial concentration levels of up to 2000 ppb showed no unknown compounds using GC or GC/MS test methods, although a few traces of C_6 and C_{12} atoms did appear on one or two reports. One possible explanation was that the concentrations of the by-products were below the detection limit. To confirm this, a 64,000 ppb concentration of TCE was prepared and irradiated. At least four by-products were found to be formed and then at least partially destroyed as the radiation dose level was increased. Chloroform and 1,1,2 trichloroethane were formed and destroyed at a dose of 275 Krads. Detectable levels of chloromethane and Methylene chloride remained at a dose of 275 krads. It appears that the higher contaminant concentration showed presence of residuals. Experiments now underway, using much larger contaminant concentrations are attempting to determine if the organic compounds are completely destroyed, forming carbon dioxide, water, and carbon or if additional by-products are formed. Preliminary results of the investigation will be included in the paper.

REFERENCES

1. J. R. Bayless, C. P. Burkhart and R. J. Adler, "Linear Induction Accelerators for Industrial Applications," Proceedings 10th International Conference on the Application of Accelerators in Research and Industry, Nov. 7-9, 1988, Denton, Texas.

2. T. D. Waite, et al., "Disinfection of Wastewater Effluents with Electron Radiation," Proc. Natl. Conf. Environ. Engin., Austin, TX, July 10-12, 1989.

3. W. J. Cooper, et al., "Treatment of Complex Mixtures of Toxic Chemicals Using an Innovative Treatment Process: High Energy Electron Irradiation," Proc. 63rd Annual Conf. Water Pollution Control Federation, Washington, D.C., October 7-11, 1990.

4. W. J. Cooper, et. al., "High Energy Electron Irradiation: An Innovative Treatment Process for the Treatment of Aqueous Based Organic Hazardous Wastes," Proc. 5th Annual Aerospace Hazardous Waste Minimization Conf., Costa Mesa, CA, May 22-24, 1990.

5. A. Singh, et al., "Radiolytic Dechlorination of Polychlorinated Biphenyls," Rad. Phys. Chem., Vol. 25, pp. 11-19, 1985.

6. P. Gehringer, et al., "Removal of Chlorinated Ethylenes from Drinking Water," Rad. Phys. Chem., Vol. 15, pp. 456-460, 1990.

7. N. Getoff and W. Lutz, "Radiation Induced Decomposition of Hydrocarbons in Water Resources," Rad. Phys. Chem., Vol. 25, Nos. 1-3, pp. 21-26, 1985.

8. M. G. Nickelsen, et al., "High Energy Electron Irradiation of Oxygenated Secondary Waste Water Effluent for the Removal of Benzene and Substituted Benzene Compounds," Proc. 198th Amer. Chem. Soc. Natl. Mtg., Miami, FL, Sept. 10-15, 1989.

9. Dr. William J. Cooper, Drinking Water Research Center, Florida International University, private communication, 11-90.

Table 2.1 Preliminary Peak G-values calculated from experimental data obtained for the deionized water experiments.

Compound	Matrix	Initial Concentration (ppb)	G_{peak}
TCE	Deionized Water	64,000	8.81
TCE	Deionized Water	2100	8.81
TCE	Deionized Water	1000	5.4
TCE	Deionized Water	490	3.52
PCE	Deionized Water	260	.61
Chloroform	Deionized Water	2000	6.1
Methylene chloride	Deionized Water	450	.054
Carbon tetrachloride	Deionized Water	180	.040
Benzene	Deionized Water	240	2.21
Toluene	Deionized Water	140	1.46
Ethylbenzene	Deionized Water	890	1.5
Xylene	Deionized Water	240	1.35

Table 2.2 Spiked well water/ethylbenzene. Preliminary G_{peak} and G_i constants calculated from the experimental data.

	R_i (mol/L)	k_i (L/mol-s)	G_{peak}	G_i Calculated	G_i Experimental
Ethylbenzene	2.57E-06	3.00E+09	1.5	1,096	0.77
Carbonate (CO_3^{2-})	2.35E-06	3.90E+08			
Bicarbonate (HCO_3^-)	2.26E-04	8.50E+06			

Table 2.3 Spiked well water/xylene. Preliminary G_{peak} and G_i constants calculated from the experimental data.

	R_i (mol/L)	k_i (L/mol-s)	G_{peak}	G_i Calculated	G_i Experimental
Xylene	2.00E-06	3.00E+09	1.35	0.917	1.13
Carbonate (CO_3^{2-})	2.35E-06	3.90E+08			
Bicarbonate (HCO_3-)	2.26E-04	8.50E+06			

Table 2.4 Superfund well water sample #1 (SFWW1). Preliminary G_{peak} and G_i constants calculated from the experimental data.

	R_i (mol/L)	k_i (L/mol-s)	G_{peak}	G_i Calculated	G_i Experimental
Trichloroethylene (TCE)	2.59E-05	4.20E+09	8.81	3.8	4.0
Perchloroethylene (PCE)	3.02E-06	2.60E+09	8.8	0.27	0.38
1,1-Dichloroethylene	4.54E-07	6.80E+09	8.8	0.11	0.087
Carbonate (CO_3^{2-})	3.00E-04	3.90E+08			
Bicarbonate (HCO_3^-)	2.20E-03	8.50E+06			

10. C. N. Kurucz, et al., "Full Scale Electron Beam Treatment of Hazardous Wastes - Effectiveness and Costs," Proc. 45th Ann. Purdue Univ. Ind. Waste Conf., W. Lafayette, IN, 5/8-10/90.

11. N. Frank, K. Kawamura and G. Miller, "Electron Beam Treatment of Stack Gases," Rad. Phys. Chem., Vol. 25, p. 35.

12. Edward H. Bryan, "Disinfection of Wastewater and Residual Sludges," Proc. Conf. on Disinfection of Wastewater, Effluents and Sludge, University of Miami, Miami, FL, May 7-9, 1984.

13. Nicesen, W. Cooper, C. N. Kurucz, T. Waite, "Removal of Benzene and Selected Alkyl Substituted Benzenes from Aqueous Solution Utilizing Continuous High energy Electron Irradiation", Environmental Science and Technology, Vol. 26, 1992.

14. Buxton, C. Creenstock, W. Helman, A. Ross "Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl radicals in Aqueous Solution, Journal of Physical and Chemical reference Data, Vol. 17, No. 2, 513-886, 1988.

RECOVERY OF LEAD BY A CHELATION/ELECTROMEMBRANE PROCESS

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INTRODUCTION

This paper summarizes the results of a bench-scale treatability test to investigate key process parameters influencing an innovative chelation-electrodeposition process in which lead is recovered while simultaneously regenerating the chelating agent. Lead-contaminated soils from battery reclamation sites typically contain 1 to 5 percent lead by weight. The forms of lead found at these sites are lead dioxide, basic lead carbonate, elemental lead, and lead sulfate.

The design of the bench-scale electromembrane reactor experiments was derived from previous soil washing studies using chelating agents and electroplating for lead recovery.(1) The goal of the recent study was to recover the lead on the cathode, at the same time regenerating the chelating agent in its sodium salt form in the cathode chamber. The chelating agents for this study were di-sodium and tetra-sodium ethylene diamine tetraacetic acid (EDTA), and diethylenetriamine pentaacetic acid (DPTA). A synthetic lead-chelate solution was tested rather than lead extracted from a contaminated soil, as soil chelation has been previously studied.(2) The lead solutions used in the tests represent the range of lead concentrations that can typically be extracted by a soil washing process employing chelating agents.

EXPERIMENTAL APPARATUS

The reactor was constructed from a 10-gallon aquarium with 1/4-inch plexiglass walls. It was divided into two chambers by the cation-exchange membrane which is almost impermeable to anions and prevents oxidation of the chelating agent at the anode. Each chamber was 2 inches long, 12 inches high, and 10 inches deep. The membrane was 7-by-7 inches and was mounted using a frame and gasketing material.

Two types of membranes were used in the study: Ionics 61AZL386 and DuPont Nafion. The Ionics membrane is a modacrylic fiber-backed cation-exchange membrane with a specific weight of 14 mg/cm2, a thickness of 0.6 mm, a burst strength of 8 kg/cm2, and a 2.7 meq/dry gram resin capacity. The Nafion membrane is a perfluorosulfonic acid cation-exchange membrane, Teflon-reinforced, with a weight of 6.3 gm/cm2, and thickness of 0.43 mm. Both membranes have low electrical resistance, high permselectivity, high burst strength, long-term resistance to aqueous acid, alkaline, and mild oxidizing solutions.

The lead electrodes were approximately 7 by 10 inches and were suspended one-inch from the membrane surface using a wooden dowel rod. In a second set of tests, cadmium electrodes were used. The electrodes were connected to a DC power supply which controlled amperage and measured both current and voltage.

EXPERIMENTAL DESIGN

The type of chelating agent, type of membrane, current density, lead concentration, and reaction time were varied to examine the effects each parameter has on lead recovery. Table 1 presents the experimental matrix for the bench-scale membrane reactor study. A total of 24 tests were performed.

Both di-and tetra-sodium EDTA and DPTA were selected for study because of their relatively high lead stability constants (18-19 @ pH=9) and prior use in soil washing studies. Based on jar tests conducted with various chelating agents concentrations, solutions of 1:1 di-sodium EDTA-to-lead molar ratio, a 1.5:1 tetra-sodium EDTA ratio, and a 2:1 DPTA-to-lead molar ratio were determined to be adequate for complete lead chelation. The forms of lead initially added in the chelant solution consisted of lead sulfate, basic lead carbonate, elemental lead, and lead dioxide. None of the lead dioxide or elemental lead was successfully chelated. Only lead sulfate and lead carbonate were used to make the synthetic lead-chelate solutions of 0.8 percent and 4 percent for the electromembrane tests.

The current densities of 15 and 25 milliamps (ma/cm2) were selected for the study. A current density above 30 ma/cm2 was previously determined to be limiting in industrial electrodialysis systems.(2) Current density is an important factor which influences the design of electromembrane reactors and power supply.

EXPERIMENTAL PROCEDURE

The cathode chamber was filled with 4 liters of lead-chelate solution adjusted to the experimental pH with sodium hydroxide or sulfuric acid. The pH values were determined for the anode and cathode chamber solutions during each experiment. Twice the stoichiometric quantity of 5 percent sodium carbonate solution (2 moles sodium per mole of lead plated is required to regenerate the sodium salt form of the chelating agent) was placed in the anode chamber to prevent depletion of sodium ions.

The electrodes were weighed and placed into the chambers approximately one-inch from the membrane. Current densities were adjusted on the power supply unit, and the reaction initiated. Samples of the anode and cathode chamber solutions were taken at 30-minute intervals for the first three hours to determine the lead plated and the depletion of sodium ions. Experiments were conducted for a total period of 3 hours to 5 hours. After the third hour, samples were taken at 1-hour intervals to obtain the optimum time required for plating out the lead. The anode chamber samples were analyzed for sodium content and the cathode chamber samples were analyzed for sodium and lead by atomic absorption.

TABLE 1. ELECTROMEMBRANE/CHELATION STUDY EXPERIMENTAL MATRIX

Chelating agent	Run No.	Current density, ma/cm^2	Lead conc., %	Membrane	Reaction time, hr	pH
Tetra-sodium EDTA	1	25	0.8	DuPont Nafion	3	9
Di-sodium EDTA	2	25	0.8	DuPont Nafion	3	9
Tetra-sodium EDTA regenerated solution[a]	3	25	0.8	DuPont Nafion	5	9
DTPA (diethylenetriamine pentaacetic acid)	4	15	0.8	DuPont Nafion	3	9
DTPA	5	25	0.8	DuPont Nafion	3	9
DTPA regenerated solution[b]	6	15	0.8	DuPont Nafion	3	9
DTPA	7	25	0.8	DuPont Nafion	5	9
DTPA	8	25	4	DuPont Nafion	3	9
DTPA	9	15	4	DuPont Nafion	5	9
DTPA regenerated solution[b]	10	25	4	DuPont Nafion	4	9
DTPA	11	15	4	DuPont Nafion	5	9
Tetra-sodium EDTA	12	25	4	DuPont Nafion	3	9
Tetra-sodium EDTA[a]	13	25	4	DuPont Nafion	3	9
Di-sodium EDTA	14	25	0.8	DuPont Nafion	3	5
Di-sodium EDTA regenerated solution[c]	15	25	0.8	DuPont Nafion	3	5
DTPA (Cadmium electrodes)	16	25	4	DuPont Nafion	3	9
DTPA (Cadmium electrodes)	17	15	0.8	DuPont Nafion	3	9
DTPA (Cadmium electrodes)	18	25	4	DuPont Nafion	3	9
Tetra-sodium EDTA (1.5% iron)	19	25	4	DuPont Nafion	3	7
Tetra-sodium EDTA (1.5% iron)	20	25	4	DuPont Nafion	3	9
Tetra-sodium EDTA (1.5% iron)	21	25	4	DuPont Nafion	3	11:5
DTPA (Ionics membrane)	22	25	4	Ionics	3	9
DTPA (Ionics membrane)	23	15	0.8	Ionics	3	9
DTPA (Ionics membrane)	24	15	0.8	Ionics	3	9

[a] Experiment was performed using the Tetra-sodium EDTA solution from runs 2 and 12.
[b] Experiment was performed using the DTPA solution regenerated from runs 4 and 9, respectively.
[c] Experiment was performed using the Di-sodium EDTA solution regenerated from run 14.

LEAD RECOVERY

The amount of lead recovered on the cathode is critical to making the electromembrane process cost-effective. Representative lead recoveries achieved by the various chelating agents (Na2 EDTA, Na2 EDTA/regenerated, Na4 EDTA, DPTA) for 0.8 percent lead and 25 ma/cm2 current density are presented in Figure 1. The highest lead removal (99.3 %) occurred when using di-sodium EDTA. The regenerated di-sodium EDTA achieved a 91 percent lead removal rate. Similar results were obtained for the tetra-sodium EDTA (not shown on Figure 1)

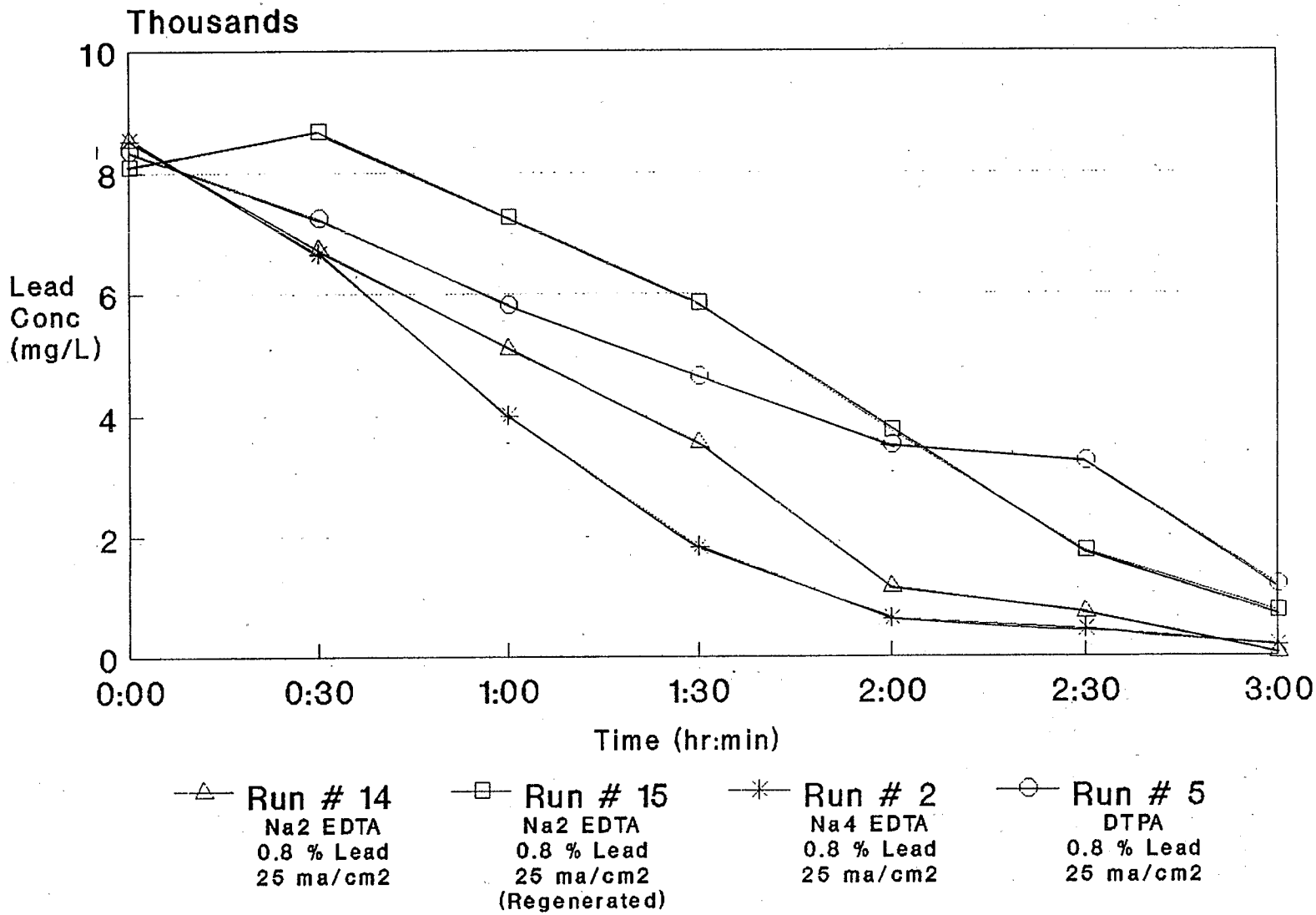
A comparison of the data obtained in the tests performed using initial target lead concentrations of 0.8 and 4 percent showed that a higher percentage of lead was recovered from the 0.8 percent lead solutions, but the mass of lead recovered was greater in the 4 percent lead tests. One possible explanation the lead removal rates were lower in the 4 percent solution tests is that the surface area of the cathode may have been "saturated", and unable to plate additional material. Additional data will be provided during the presentation.

REFERENCES

1. PEI Associates, Inc. Innovative Electromembrane Process for Recovery of Lead from Contaminated Soils. National Science Foundation Grant No. ISI-8560730. July, 1986

2. Assessment of Current Treatment Techniques at Superfund Battery Sites. Bureau of Mines. W. Schmidt. 1990

Figure 1. Comparison of Lead Removal for Three Chelating Agents



ULTRAVIOLET LIGHT DEGRADATION OF POLYCHLORINATED BIPHENYLS

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INTRODUCTION

Polychlorinated biphenyls, PCBs, and other chlorinated aromatic compounds have had widespread industrial usage during the past years due to their chemical and thermal stability and excellent dielectric properties (1,2,3,4,5,6). Currently, they are illegal for most applications and are being phased out of others. Highly chlorinated PCB congeners have been implicated as carcinogens and mutagens, and all congeners are thought to alter liver functions and negatively impact longevity (1,7). Ironically, the desirable properties of PCBs, which made them so desirable for industrial and commercial applications are the properties now responsible for their long term persistence in the environment (1,8,9).

There have been many approaches to treating PCB contaminated waters using ultraviolet light. Degradation of organics can be induced by exposure of the target compound to electromagnetic radiation of a wavelength which the compound absorbs. With sufficient overlap, light may be used to effect the photolytic reaction directly. For poor spectral overlap, the degradation can be induced, for example, using hydrogen peroxide as a radical initiator in the presence of light (10). Additionally, the light can be used indirectly with a variety of chemical sensitizers or surfaces that enhance the rate of degradation by offering a more efficient and/or less energetic pathway (11,12,13).

The photolysis of PCBs has been studied for over twenty years. Many of these studies were carried out using natural solar radiation ($\lambda > 290$ nm) or artificial light sources that emit continuous radiation in the same region of the electromagnetic spectrum (4). The environmental fate of PCBs contaminating the environment was the focus of these early research activities utilizing sunlight. The results of these environmental fate studies show that limited amounts of dechlorination occurred, and that the more highly chlorinated congeners are the most susceptible to the dechlorination. Additionally, for long exposure times in natural systems, undesirable condensation products were identified. The results led to the conclusion that minimal degradation of PCBs contaminating air, water, and soil environments could be expected from the natural interaction with sunlight. Unfortunately, the lowest wavelength emitted by the light sources used in the fate experiments, including the sun, overlap only the low energy tail of the primary absorption band of the substituted biphenyls. This poor overlap of the light source and the absorption bands of the target compounds results in very inefficient and very slow photolysis.

Specific results of early photolysis studies of PCBs include some product identification and rate information. Degradation experiments performed in methanol produced methoxylated products via nucleophilic substitution (5,13). Results of sensitized photodegradation produced similar products (14,15). Photolysis in water yielded hydroxylated biphenyls and perhaps some ethers, including the more toxic dibenzofurans and dioxins (6,16). The low solubility of PCBs in water often necessitates the addition of an organic co-solvent and acetonitrile has been used most often (3). Condensation products have also been identified as products in some of the longer exposure time experiments (6). The rates of the degradation in these experiments were on the order of hours to days.

The objectives of this research are to investigate the feasibility of using direct photolysis for the degradation of PCBs at discrete wavelengths between 185 and 266 nm. At these wavelengths, direct photolysis should be enhanced due to the increased overlap of the source radiation and the absorption band of the target chemical. Most PCB's have ultraviolet absorption bands near those of unsubstituted biphenyl, which absorbs strongly at 202 and 248 nm. The main thrust of this work is to understand the influence of the operating parameters (wavelength, exposure time, and power level) in aqueous solutions, organic solvents, and in pure compound phases, on degradation rates, efficiencies, and final photoproducts. Photolysis kinetics and mechanisms were determined as necessary in support of developing optimal operating conditions.

METHODOLOGY

All PCB congeners were obtained in the purest forms commercially available from Ultra Scientific Co. Stock solutions (0.00026 M) of the PCBs (2-chlorobiphenyl, 3,4-chlorobiphenyl, 2,2'-dichlorobiphenyl, 2,2',6,6'-tetrachlorobiphenyl, and 2,2',4,4',6,6'-hexachlorobiphenyl) were prepared in spectral grade methanol and acetonitrile purchased from Mallinkcrodt. Aqueous solutions were prepared as needed in distilled deionized water (Millipore-Waters mill-Q) water at concentrations near saturation of the individual congeners.

The output power of the mercury lamp was measured with a Newport Corp. Model 815 power meter with ultraviolet sensitive photodiode. A bandpass filter passed only the 254 nm line. Some mercury lamp experiments used a colored glass filter to pass the 254 nm line and exclude the 185 nm line. Such experiments are termed filtered lamp experiments. The mercury lamp power was also determined by ferrioxalate actinometry (17). Although low pressure mercury lamps are characterized predominately by emission at 254 nm, they are also known to emit small amounts (<1%) of 185 nm light (18).

The photolysis experiments of 3 ml samples of solution phase PCBs were conducted as continuously stirred, batch experiments in a one centimeter square suprasil quartz cuvette, (Spectra Cell). Mercury lamp photolysis was performed at a distance of one centimeter from the lamp and laser experiments at convenient distance inside the focal point of the focused laser beam. The latter distance was adjusted so that the laser beam profile would be the same size as the cuvette containing the PCB solution. The filtered mercury lamp experiments were run with the 185 nm absorbing filter placed directly between the sample cuvette and the mercury lamp. During the photolysis experiments, 200-microliter samples were taken at timed intervals for analysis.

Samples were analyzed as soon as possible after photolysis for the starting PCB congener, unsubstituted biphenyl, as well as substitution and rearrangement products using a Hewlett Packard, HP 5890 Series II gas chromatograph, with a 30 meter x 0.53 mm (id) DB-1 column (J&W Scientific Co.) column fitted with an HNU photoionization (PID), and/or a 30 meter x 0.53 mm (id) DB-5 column (J&W Scientific) with an electron capture detector (ECD). Ultraviolet spectra and absorption measurements were made on a Varian DMS 200 Ultra Violet Spectrophotometer. Mass spectra were obtained using a Finnigan MAT INCOS 50 Mass Spectrophotometer interfaced to an HP 5890 gas chromatograph with a 30.0 meter x 0.24 mm (id) DB-5 column.

Unfiltered mercury lamp (185 and 254 nm) experiments were performed on the stock solutions of individual congeners: 2-chlorobiphenyl, 3-chlorobiphenyl, 4-chlorobiphenyl, 2,4-dichlorobiphenyl, 2,4'-dichlorobiphenyl, 2,2'-dichlorobiphenyl, 2,2',6,6'-tetrachlorobiphenyl (tetPCB), and 2,2',4,4',6,6'-hexachlorobiphenyl (HexPCB) in either acetonitrile or methanol. Additionally, 2-chlorobiphenyl was photolyzed in water. Small amounts of acetonitrile or methanol were added to aqueous samples to increase the solubility.

Aqueous degradation experiments on 2-chlorobiphenyl were monitored by observing changes in the uv spectrum during the reaction. Loss of the biphenyl ring structure's absorbance band near 250 nm as well as the growth and decay of the smaller secondary absorbance band near 270 nm of the hydroxylated product were followed. The degradation appears to be complete in less than 10 minutes, and the rate constant is approximately 0.398 min-1. Photolysis of the 2-chlorobiphenyl in water was also monitored using a HPLC with UV and fluorescence detectors. The degradation rate of the congener was 0.635 min-1, slightly faster than the degradation in pure methanol.

RESULTS

This presentation will summarize and discuss the rate data for the photolysis of chlorinated biphenyl congeners in water, methanol, and acetonitrile using the 254 nm and 185 nm light of the mercury lamp. The first order rate constants varied with solvent and wavelengths from a maximum of 0.7074 to 0.0094 minutes^{-1}. Experiments using the laser as the light source with wavelengths of193, 248, and 266 nm produced first order rate constants ranging from 0.101 to 3.30 joules^{-1}. Results of several mechanistic experiments also confirmed the reaction pathways to be homolytic or heteolytical cleavage depending upon the solvent system.

CONCLUSIONS

Direct photolysis of methanolic solutions of low chlorinated PCB congeners using the low pressure mercury lamp with a primary emission at 254 nm occurs through a highly efficient heterolytic cleavage of the carbon-chlorine bond. Alternatively, direct photolytic degradations in acetonitrile occur via a homolytic cleavage at a considerably slower rate. The fastest degradation occurred in water, however, this occurred only slightly faster than that in pure methanol, and small amounts of methanol were added to increase the solubility of 2-chlorobiphenyl in the water. The primary photoproducts are the same that have been identified previously by others for direct photolysis of these same congeners under exposure to longer wavelength (>290 nm) radiation. Low wavelength photolysis occurred much faster than previously reported rates at these longer wavelengths.

Comparison of mercury lamp filtered and unfiltered experiments reveal some decline in the photodegradation rates for experiments on the same congener. Rate constants were lowered an average of 35%, which includes approximately 10% attenuation by the optical filter itself. Photodegradation experiments with a monochromatic source with an output only near 185 nm and having approximately the same power, should help elucidate the effects, if any, of this emission from the low pressure mercury lamp. Lack of significant degradation of 2-chlorobiphenyl and other congeners using the ArF excimer laser (193 nm) suggest that the methanol and acetonitrile used as solvents were absorbing much of this low wavelength light, regardless of its intensity. Using the KrF excimer laser with emission at 248 nm or low pressure mercury lamp with emissions at 254 nm and 185 nm, very efficient degradation was achieved in all solvents. Finally, destruction of the biphenyl ring structure has been observed during the short wavelength photolysis, indicating a more extensive breakdown of the parent chlorinated biphenyl.

REFERENCES

1. Hutzinger, O., S. Safe, and V. Zitko, 1974, The Chemistry of PCBs, CRC Press, Cleveland, Ohio.

2. Safe, S., O. Hutzinger, 1971, "Polychlorinated Biphenyls: Photolysis of 2,2',4,4',6,6'-

3. Bunce, N. J., 1982, "Photodechlorination of PCBs: Current Status,"Chemosphere, 11: 8, 707-714.

4. Bunce, N.J., and Y. Kumar, 1978, "An Assessment of the Impact of Solar Degradation of Polychlorinated Biphenyls in the Aquatic Environment," Chemosphere, 11: 2, 155-164.

5. Ackerman, D. G., 1983, "Destruction and Disposal of PCBs by Thermal and Non-Thermal Methods," in Pollution Technology Review, No. 97, Noyes Data Corporation.

6. Epling, G. A., E. M. Florio, A. J. Bourque, X. Qian and J. D. Stuart, 1988, "Borohydride, Micellar, and Exciplex-Enhanced Dechlorination of Chlorobiphenyls," Environ, Sci and Technol., 22:952-956.

7. Brown, J. F., 1992, "The Human Health Effects of PCBs: Update '91", Proceedings: 1991 EPRI PCB Seminar, Baltimore, MD.

8. Hallet, D., 1988, "Ecosystem Management of Persistent Toxic Contaminants and Ecosystem Health: Back to Basics," in Toxic Contaminants and Ecosystems Health: A Great Lakes Focus, John Wiley and Sons, New York, New York.

9. Simmons, M., 1984, "PCB Contamination in the Great Lakes," in Toxic Contamination in the Great Lakes, John Wiley and Sons, New York, New York.

10. Bull, R. A. and J. D. Zeff, 1991, "Hydrogen Peroxide in Advanced Oxidation Processes for Treatment of Industrial Process and Contaminated Groundwater," in Proceedings: First International Symposium on Chemical Oxidation: Technologies for the Nineties, Technomic Publishing Co., Nashville, Tennessee.

11. Ollis, D. F. and C. Turchi, 1990, "Heterogeneous Photocatalysis for Water Purification: Contaminant Mineralization Kinetics and Elementary Reactor Analysis," Environmental Progress, 9:4, 229-234.

12. Ollis, D. F., E. Pelizzetti and N. Serpone, 1989, "Heterogeneous Photocatalysis in the Environment: Application to Water Purification," in Photocatalysis: Fundamentals and Applications, John Wiley and Sons, New York, New York.

13. Safe, S., N. J. Bunce, B. Chittim, O. Hutzinger, and L. O. Ruzo, 1976, "Identification and Analysis of Organic Pollutants in Water," in Photochemistry of Bioactive Compounds. Photodecomposition of Halogenated Aromatic Compounds, Ann Arbor Press, Ann Arbor, Michigan.

14. Bunce, N. J., 1982, "Photolysis of Aryl Chlorides with Aliphatic Amines", J. Organ. Chem., 47, 1948-1955.

15. Epling, G. A., Q. Wang and Q. Qiu, 1991, "Efficient Utilization of Visible Light in the Photoreduction of Chloroaromatic Compounds," Chemosphere, 22:9-10, 959-962.

16. Crosby, D. G. and K. W. Moilanen, 1973, "Photodecomposition of Chlorinated Biphenyls and Dibenzofurans," Bull. Environ. Cont. and Toxicol., 10:6, 372-377.

17. Hatcher, C. G., and C. A. Parker, 1956, Proceedings of the Royal Society of London Series A, 235, 518-536.

18. Rabek, J. F., 1982, Experimental Methods in Photochemistry and Photophysics, Part I, John Wiley and Sons, New York, New York.

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REMEDIATION OF METAL-CONTAMINATED SOIL BY ELECTRIC FIELDS

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INTRODUCTION

In electric-field restoration, electrodes are placed in the contaminated soil and a direct-current (dc) potential is applied across them (1). The electric field drives the contaminants to the electrode wells from where they can be brought to the surface. The process is essentially one of soil flushing, but has several advantages over the usual pressure-driven pumping process. For example, the transport rate induced by an electric field is not reduced by decreasing soil permeability, and the path followed by the contaminants is confined by the electric field to the region between the electrodes. Electric-field restoration can consequently be used in soils of low or variable permeability and in situations where precise control over the movement of the contaminants is required.

The electric field drives the contaminants toward the electrodes by two mechanisms. One is electroosmosis, an electrokinetic phenomenon, in which the saturating liquid and dissolved substances flow toward an electrode. The electroosmotic flow rate is proportional to the applied electric field strength and the charge difference or "zeta potential" across the soil-liquid interface. The value of the zeta potential is very sensitive to soil properties and the composition of the saturating liquid. Water in silt and clay formations typically has a zeta potential of -10 to -100 mV, and on application of a 100 V/m electric field will flow toward the cathode at a velocity of the order of 10 cm/day.

If the dissolved contaminants are ionic and carry a charge, then they will experience a force in the electric field that will result in an additional velocity being imposed upon them. This *electromigration* velocity is proportional to the product of the applied electric field and the charge on the ions. Because metal containing wastes typically have high ionic strengths which suppress the zeta potential, electromigration may be the dominant or only transport mechanism when treating heavy metal wastes.

Removal of heavy metals by electromigration might be expected to be a relatively straightforward process. The velocity of the ions is generally from one to several orders of magnitude higher than the electroosmotic flow, and is not affected by variations in the zeta potential and soil type. However, laboratory tests have indicated that whereas removal of dissolved organic (uncharged or only weakly dissociated) molecules by electroosmosis is invariably successful, poor removal efficiencies are sometimes obtained with metal wastes.

In this paper, the results of an experimental investigation in which zinc is removed from clay are presented to highlight the anomalous results that may be obtained with metals. The underlying physics leading to the poor removal is then discussed, and means of attaining high removal efficiency described. A mathematical model is then developed to simulate the metal removal process, and is solved numerically.

Much of this work has appeared or will appear in other publications (1-3).

METHODOLOGY

Experiments were conducted to evaluate the effect of the changes in soil pH that occur during the electrorestoration process on the efficiency of metal removal. Georgian kaolin clay was saturated with a 500 mg/L zinc solution, placed in a 20 cm long Plexiglas tube, and held in place by stainless steel screens covered with filter paper. The tube was then connected on each end to an electrode well containing carbon electrodes across which a d.c. potential was applied. The stainless steel screens served as reference electrodes for measuring the potential drop across the soil. Plastic tubing connected the electrode wells to reservoirs which contained the purge solutions and rinses. Pressure induced flow through the soil was prevented by equalizing the static heads in the connecting tubing. Ports in the electrode wells vented the oxygen and hydrogen produced by the electrolysis of water at the carbon electrodes.

The pH of the saturating solution was adjusted to 6 with sodium hydroxide solution. As a result, the solution had a relatively high concentration of sodium ions (~0.1M). In some experiments, pH-indicators were added to visualize pH changes in the clay. The saturated clay was allowed to equilibrate for one day before the prepared sample was placed in the Plexiglas cylinder using a vibrating table. The system stood for another day before applying the electric field. The experiments were run with a constant voltage of 20 V across the clay as measured at the reference electrodes. Most experiments were run for about 9 days. During the experiment, the volume of fluid collected in the cathode reservoir was monitored as well as the current through the cell and the voltages across the reference and working electrodes. Samples were withdrawn periodically from the electrode wells for determination of pH and dissolved zinc concentration. Zinc concentrations were determined using a high pressure liquid chromatograph or a spectrophotometer.

At the end of each run the anode and cathode solutions were analyzed for dissolved and total zinc. In addition, the clay was divided into ten sections and each section analyzed for its pH, average zinc concentration and liquid fraction. The pH was estimated by placing a pH-paper in contact with the clay. To determine the average dissolved zinc concentration, the pore solution was separated from a portion of a clay section by centrifugation. Another portion of the clay sample was acidified with nitric acid before centrifugation for determining the total zinc concentration. The water content was determined by comparing the weight of the remaining clay section before and after drying in an oven.

To model the process, the convective diffusion equation was solved numerically. For 1-D flows, the overall transport rate for species i is:

$$\frac{\partial C_i}{\partial t} = \frac{D_i}{\tau^2}\frac{\partial^2 C_i}{\partial x^2} + \frac{1}{\tau}\frac{\partial}{\partial x}\left[\frac{\nu_i z_i F C_i}{\tau}\frac{\partial \phi}{\partial x} - C_i u_c\right] + R_i + R_i^a \qquad (1)$$

where C is the concentration, D the diffusion coefficient, τ the tortuosity, z the charge number, ν the mobility, F the Faraday constant, ϕ the voltage, u_c the convection velocity, and R_i and R_i^a are the molar rates of production due to chemical reactions and sorption, respectively. The first term inside the brackets is the molar flux due to electromigration and the second term is the molar flux due to convection. This convective transport originates from the electroosmotic flow. The rate of transport due to diffusion is normally negligible relative to migration and osmosis, except in locations where very steep concentration profiles develop.

There are usually a number of chemical species that have to be considered in electric field restoration. These include the contaminants and co-contaminants that have percolated from the surface, as well as naturally occurring substances such as soil electrolytes, carbonates, and humic materials. These substances affect the transport process by modifying the electrical properties of the media, and most of

them participate in chemical reactions. Reactions include dissociation, for example of water or a weak organic acid, into ions, sorption onto the soil, and complexation or precipitation reactions.

The sorption rate, R_i^a, is essentially a constraint characterized by a particular isotherm, and it relates the concentration in the adsorbed phase to that in the bulk solution. The reaction rate, R_i, is eliminated from the equation by using the equilibrium constant for the reaction and the conservation of mass of the elements to determine the equilibrium concentration of the species. The equilibrium assumption is justified in that the time constants of the reactions and sorption processes are normally much smaller than the transport time constants. This may not be valid for dissolution of precipitates.

After satisfying the electroneutrality condition, $\Sigma z_i C_i = 0$, there are two unknowns remaining in Eq.(1), namely the electric field and the convection velocity. The electric field is obtained from the equation for the current density, i

$$i = -\frac{1}{\tau}\frac{\partial \phi}{\partial x} F^2 \Sigma z_i^2 \nu_i C_i - \frac{F}{\tau} \Sigma z_i D_i \frac{\partial C_i}{\partial x} \qquad (2)$$

The current remains constant along the length of the cell, so the electric field varies with position to compensate for variations in concentration. Because the total applied voltage is known, Eq.(2) provides a relationship between $\partial\phi/\partial x$ and C_i.

At the electrodes, species are oxidized or reduced with release or capture of electrons from the external circuit. The rate of the electrode reactions is fixed since the current in the electrolyte (flow of ions) must match the current in the external circuit (flow of electrons). In the usual case of inert electrodes in which the electrode reaction is the electrolysis of water to produce hydrogen (anode) or hydroxyl (cathode) ions, the reaction rate and the current need not be known. Instead, the concentration of hydrogen and hydroxyl ions is obtained from the electroneutrality condition.

The second unknown, u_c, is constant in space and is given by

$$u_c = \frac{\epsilon}{\tau\mu} \langle \zeta \frac{\partial \phi}{\partial x} \rangle \qquad (3)$$

where ϵ is the permittivity of the fluid, μ its viscosity, ζ the zeta potential, and < > denotes a volume average. In the zinc experiments, the convection velocity was small and does not significantly affect the overall metal transport.

RESULTS

Electrolysis of water occurred at the electrodes, with hydrogen ions being produced at the anode and hydroxyl ions at the cathode. The pH was found to reach its final value of around 1 at the anode, and about 12 to 13 at the cathode, within the first 15 minutes of a run, and then to remain essentially constant. The hydrogen and hydroxyl ions produced by electrolysis migrated into the soil as waves of low and high pH. The velocity of both fronts remained fairly constant, with that of the acid front measured at 0.56 m/day, which is 1.9 times the 0.28 m/day measured for the alkaline front.

The measured distribution of pH and total (dissolved plus precipitated) zinc in the clay at the end of a 9-day run is shown in Figure 1. The steepness of the pH jump and its influence on the zinc distribution can be clearly seen. Near the anode the zinc is at a relatively low concentration and is in the dissolved state. Near the cathode the pH is high so the zinc is present as the hydroxide precipitate in amounts

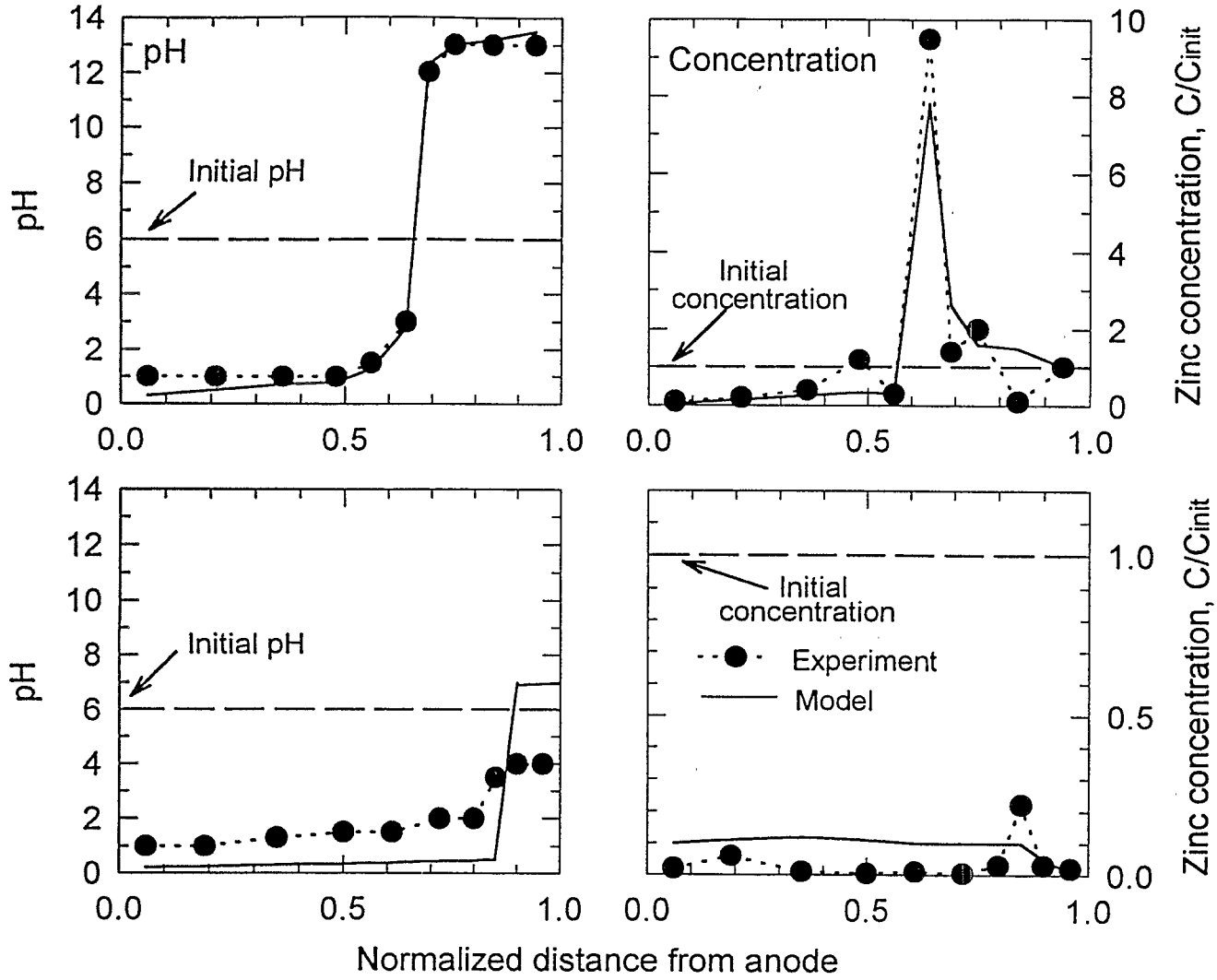

Figure 1. Distribution of pH (left) and total zinc concentration (right) after a 9-day test. Top: Without electrode rinse. Bottom: Cathode rinsed with tap water.

approximately equal to the initial concentration. Some 40 to 60 percent of the original zinc is found precipitated in a narrow band at the position of the pH jump, where its concentration reaches some 10 times the original concentration. The measured removal efficiencies were poor at from 2 to 10 percent.

To eliminate this isoelectric focusing effect (1), the hydroxyl ions must be prevented from entering the soil. This can be achieved by rinsing them away or neutralizing them as they are formed, or by promoting conditions for an alternative electrode reaction that does not produce hydroxyl ions. In our experiments, the hydroxyl ions were simply rinsed away with tap water. This kept the pH at the cathode neutral with only slight increases at the beginning of the experiment due to the initially high currents. This process of rinsing the electrodes enhanced the zinc removal efficiency to 98%. The final pH and zinc distributions in the clay for the case of the cathode rinse are also shown in Figure 1. The pH is reduced to below 2 throughout most of the soil, and only approaches its maximum value of 4 at the cathode. The measured zinc concentration is everywhere less than one-quarter its initial value.

The numerical solutions to Eq.(1) indicate that very sharp changes develop in the pH and species concentration profiles. These kinematic wave fronts are formed because of the very limited role of molecular diffusion relative to electromigration and convection. Due to its small length scale, the diffusion term is important only in the vicinity of the discontinuities. To simulate this effect properly, the length scale of the computational elements had to be very small. In addition, the time increment also has to be reduced considerably to avoid numerical instabilities.

The numerical solutions are included in Figure 1. To simulate the electrode rinse, the pH at the cathode was fixed at pH 7. As can be seen, the mathematical model shows good agreement with the experimental data for both the rinsed and unrinsed cases.

CONCLUSIONS

When the cathode was not rinsed, the zinc was not removed from the soil but concentrated at an intermediate point between the electrodes by a process known as isoelectric focusing. The focal point coincides with the pH of minimum solubility of the metal, and occurs at the position where the pH increases sharply.

Application of the model identified the physical phenomena that importantly effect metal removal efficiencies. The value of the pH on either side of the jump is dependent on the concentration of soluble ions present in the saturating solution. These ions migrate and accumulate near the electrodes. To satisfy electroneutrality, hydrogen ions accumulate with the anions, and hydroxyl ions accumulate with the cations. In the presence of a metal contaminant, the increase in pH in the cathode region is buffered to some extent by consumption of the hydroxyl ions to form the hydroxide precipitate. As the pH increases further, the precipitate may redissolve to produce, typically, negatively charged hydroxo complexes and hydrogen ions, further buffering the pH rise. The metal cations and negatively charged complexes migrate toward each other and precipitate at the position of the pH jump.

The conductivity is also dependent on the concentration of ions in the saturating solution. It is relatively high everywhere in the clay excepting at the position of the pH jump where it is very low. At this position, the hydrogen and hydroxyl ions are at their minimum values, the metal ions have precipitated, and other soluble ions have migrated toward the electrodes. Consequently, the electric field is very high in the region of the pH jump. The growth of the electric field is relatively unstable because any ions in this region migrate away rapidly under the action of the increasing field strength.

Both the model and experiment show that problems related to isoelectric focusing can be prevented by simply rinsing away the hydroxyl ions generated at the cathode, resulting in better than 98 percent zinc removal. To simulate specific site conditions, the model must be extended to include the chemistry of soil electrolytes, organic matter, and co-disposed substances, and should also include thermal effects.

REFERENCES

1. Probstein, Ronald F. and Hicks, R. Edwin. Removal of contaminants from soils by electric fields. Science. 260: 498-503, 1993.

2. Jacobs, Richard A., Sengun, Mehmet Z., Hicks, R. Edwin and Probstein, Ronald F. Model and experiments on soil remediation by electric fields. Paper presented at Emerging Technologies in Hazardous Waste Management V, American Chemical Society, Atlanta, Georgia. September 27, 1993.

3. Hicks, R. Edwin and Tondorf, Sebastian. Electrorestoration of metal contaminated soils. To be submitted to Environ. Sci. Technol. 1994.

FATE OF TERPENES IN THE ACTIVATED SLUDGE PROCESS

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INTRODUCTION

Chlorinated solvents are used extensively throughout industry for metal and printed circuit board cleaning applications. The U.S. Environmental Protection Agency's (EPA) Office of Pollution Prevention and Toxics, previously known as the Office of Toxic Substances, has been investigating alternative materials for metal and printed circuit board cleaning applications because of the potential adverse environmental and occupational health effects associated with chlorinated solvents. Terpenes and certain aqueous cleaners have been found to have potential for replacing chlorinated solvent usage in many cleaning applications. Recently, the industrial demand for these alternative cleaning materials has risen sharply.

The use of terpenes is anticipated to have many environmental and occupational health advantages over chlorinated solvents; however, the fate of these compounds in wastewater treatment processes is largely unknown. Concerns regarding the potential aquatic toxicity of these compounds and their anticipated increase in usage as solvent substitutes prompted EPA to sponsor this study of terpene fate in the activated sludge process.

METHODOLOGY

Blank Activated Sludge Test with d-limonene

During this test, terpene laboratory analytical methods were tested and verified through a "blank activated sludge test", wherein the pilot-scale activated sludge unit does not contain biomass but is fed with tap water spiked with dilute concentration of a terpene-based cleaner. DUSQUEEZE, a citrus-based industrial cleaner containing d-limonene, was used for the tests. Operation in a "blank activated sludge test" mode eliminated biodegradation as a removal mechanism. Therefore, the validity of the liquid and air measurement techniques were verified by monitoring the pilot systems inlet and outlet streams and performing a material balance by comparing the sum of the outlet streams with the quantity measured in the inlet. Specifically, the analytical techniques were successful in providing mass balance closure within 10% around the aeration basin of the pilot scale activated sludge system.

Three pilot-scale activated sludge units were operated using 0.5 L/min of municipal wastewater from the City of Cincinnati spiked with terpene-based industrial cleaners.

Fate of d-Limonene in Wastewater

Operation of three pilot-scale activated sludge systems was initiated in late October 1992, and has continued to the present. The units were allowed to acclimate to the d-limonene for approximately two months. Performance of the activated sludge unit was monitored through analyses of effluent total suspended solids (TSS) levels and total chemical oxygen demand (COD) removal efficiencies. Monitoring of d-Limonene fate was officially initiated in January 1993 and lasted one month. All d-limonene analyses were performed utilizing a gas chromatograph at the T&E Facility.

CONCLUSIONS

The following conclusions were drawn from the analysis of the data collected from the three activated sludge units in January 1993:

- Greater than 95% of the d-limonene was removed from the typical activated sludge process at wastewater influent concentrations less than 10 mg/L. Removals greater than 99% were achievable. D-limonene discharge concentrations below 10 μg/L were typical.

- The primary method of d-limonene removal from a typical activated sludge process was biodegradation. Between 47 and 81% of the d-limonene entering the primary clarifier could be biodegraded. Between 55 and 95% of the d-limonene entering the aeration basin could be biodegraded.

EXPERIMENTAL AND DETAILED MODELING STUDIES OF PYROLYTIC AND OXIDATIVE PROCESSING OF CHLOROCARBON / HYDROCARBON SYSTEMS

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INTRODUCTION

Incineration is a viable, but often ill perceived hazardous waste disposal option. In order to optimize incinerator performance and allay public fears, a fundamental understanding of the chemical and physical mechanisms of waste combustion is needed. This is especially true for chlorinated hydrocarbon (ClHC) waste incineration, where concerns include flame stability, formation of products of incomplete combustion (PIC's), and economy of operation.

The ClHC-induced combustion instability has at least two consequences. The first is the formation of PIC's. During periods of intermittancy, high levels of unburned hydrocarbon (HC) and ClHC are emitted. The second is the supplemental amounts of expensive HC fuel required to maintain flame stability and temperature in the presence of ClHC.

There is a need for improved incinerator design, especially regarding afterburners. Conditions in the upstream rotary kiln incinerator are often difficult to control, so the downstream afterburner is critical for prevention of PIC's. There is a need to determine the mechanism of a PIC emission; i.e., either from a chemical constraint or a mixing constraint. Our study will contribute to this understanding. In addition, there is a need to influence Federal regulations regarding afterburner design and regulation to reflect the recent findings regarding issues such as inhibition.

OBJECTIVES OF THIS RESEARCH

Our **objectives** are: a) to perform well characterized experiments on the oxidative and pyrolytic reactions of ClHC characteristic of those found in incinerator environments, b) to perform well characterized experiments on the effects of trace quantities of ClHC and their oxidation products (primarily HCl) in typical post-combustion conditions, c) to develop detailed comprehensive reaction mechanisms for the oxidation and pyrolysis of ClHC, d) to determine the fundamental pathways of ClHC-induced inhibition of HC/air combustion, e) to utilize knowledge obtained in the above tasks to construct applied models for designing and optimizing incineration processes, and f) to apply these mechanisms and applied models to characterize a large scale afterburner.

APPROACH

Experiments at NJIT have been performed on two devices: 1) Externally heated tubular flow reactors with stable species sampling and analyses by gas chromatography (GC), and 2) a Laminar flat flame with a laser induced fluorescence diagnostic for free radical measurements, plus stable species sampling and analyses by GC. Detailed reactions mechanisms have been constructed which are

based on fundamental thermochemical kinetic principles. The mechanisms have been used in plug flow reactor and premixed flat flame computer simulations to model the observed species profiles obtained in our experiments. Further modeling has identified the key reaction pathways for chlorocarbon inhibition. A complex model (based upon groupings of idealized reactors) has been constructed for used with NJIT mechanisms to characterize a large scale incinerator afterburner at the EPA Air and Energy Engineering Research Laboratory in Research Triangle Park.

TUBULAR FLOW REACTOR STUDIES

Experimental research with the isothermal NJIT tubular flow reactors has been completed for reactions in the following ClHC/HC/oxygen systems:

i. Oxidation of Chloromethane / Methane / Oxygen Mixtures
ii. Oxidation of Methylene Chloride / Methane / Oxygen Mixtures
iii. Pyrolysis and Oxidation of Chloroform and Chloroform / Methane Mixtures
iv. Pyrolysis and oxidation of 1,1,1, Trichloroethane (111T)

Recent research is on the mixed reaction system: $CH_2Cl_2/CH_4/Toluene/O_2$. Data is typically collected at one atm absolute pressure between the temperatures of 680 to 840 C (953 to 1113 K), at residence times from 0.2 to 2.0 seconds.

LAMINAR FLAT FLAME STUDIES

Experimental and modeling work in our laboratories has provided the foundation for a novel hypothesis to explain ClHC-induced hydrocarbon/air flame inhibition. A major component of the hypothesis is that combustion-generated hydrogen chloride (HCl) inhibits the conversion of carbon monoxide (CO) to carbon dioxide (CO_2) by consuming hydroxyl radical (OH). The work performed with the flat flame is designed to further test this hypothesis.

The experimental research with the laminar flow **flat flame** has been conducted with the methane/methylchloride/air systems at both fuel-lean and fuel-rich feeds. Experimental data from stable species probe sampling and GC analyses have been obtained from these flames. Results show that the molar CO/CO_2 ratio increases as the chlorine content of the feed increases (for constant ϕ), which is consistent with the inhibition hypothesis.

Rate-of-production (pathway) analyses of the modeling results, all of which utilize the mechanisms developed in this and the previous projects as described below, have been performed. These results support the hypothesis that OH depletion, and hence flame inhibition, occurs primarily via reaction with flame-generated HCl. In addition, especially in the fuel rich flames, H is also consumed by HCl to form H_2, which also consumes OH. This represents a fundamental shift of the product slate from CO_2 to H_2O.

Relative OH concentration profiles have been generated for one each of the fuel-lean and rich flames listed above (no CH_3Cl and CH_3Cl/CH_4 = 0.25) by laser induced fluorescence (LIF) in these flames. The process required to convert raw data signals to relative concentrations is difficult, requiring consideration of the rotational partition functions and collisional quenching rates, both of which are temperature dependent. We have found that accurate and spatially precise thermocouple temperature profiles are difficult to make in this atmospheric pressure flame. We are working to improve the reliability

of the temperature data. In addition, work is continuing in regard to a correct spectral interpretation of the LIF data.

THERMOCHEMICAL DATABASES DEVELOPMENT

Thermodynamic databases, developed at NJIT for use in reaction mechanisms to model oxidation and pyrolysis, now include:

i) Chloro and dichloro methane plus chloro and dichloro ethane oxidation in hydrogen, methane and or ethane co-fired fuels.
ii) Chloroform and Carbon Tetrachloride in H_2, CH_4 and/or C_2H_6 co-fired fuels.
iii) Highly Chlorinated Ethanes - tri chloro to hexachloro ethanes in hydrogen, methane and / or ethane co-fired fuels
iv) Chlorobenzene and benzene in H_2, methane and / or ethane co-fired fuels.
v) Dibenzofurans and dioxins, Chlorinated Dibenzodioxins and Furans.

The NJIT Chlorocarbon Thermochemical Property Database has been significantly improved. The Group additivity technique has been modified to include interaction groups for both substituents on aromatic rings as well as multiple chlorines on adjacent carbons of chloroalkanes and chloroalkenes. The improvement in our group additivity scheme with the use of only four interaction groups is also exhibited in the entropies and heat capacities (temperatures from 298 to 10,000 K). A second improvement is in the database for PCDDs and PCDFs. Here we have developed a database complete enough to allow equilibrium and mechanism calculations for PCDD/Fs.

NJIT DETAILED ELEMENTARY REACTION MECHANISMS

Our reaction mechanisms, each ranging from 200-300 elementary reactions and 60-80 species, developed and validated against NJIT lab flow reactor experiments plus literature data where available, applicable for use in modeling oxidation, pyrolysis, and combustion/incineration processes. Our mechanisms are based upon the fundamental principles of transition state theory, molecular thermodynamics, thermochemical kinetics, group additivity, and Quantum Rice-Ramsberger-Kassel (QRRK) theory. A key goal in our developments is the applicability of the mechanism beyond range of its experimental calibration.

We have developed detailed mechanisms for:

i) Pyrolysis and Oxidation of Chloromethane and/or Methylene Chloride/Hydrogen / Methane / Oxygen Mixtures
ii) Pyrolysis and Oxidation of Chloroform and Carbon Tetrachloride - hydrogen / Methane Mixtures
iii) Pyrolysis and oxidation of Tri, tetra, penta and hexachloro ethanes.
iv) A Benzene / Chlorobenzene oxidation and pyrolysis. This mechanism is still in validation and expansion / refinement, as we continue to learn about the pyrolysis and oxidation reactions of aromatics such as benzene.

These mechanisms are primarily for combustion applications. They have pressure dependent rate constants, which, though published for 1 atmosphere combustion conditions, are known at different pressures. One limitation of the mechanisms is the lack of molecular weight growth above C_2 species. (One exception here is the benzene / chlorobenzene system which is still under development).

We have completed a significant number of modifications and extensions to our

benzene and chlorobenzene oxidation and pyrolysis reaction mechanism. The current mechanism is now validated against experimental reaction data for chlorobenzene pyrolysis and oxidation from our own laboratory and from four other laboratories.

The mechanism generates model predictions which are in excellent agreement with data on CO production from anisole pyrolysis reported by Lin. Similar excellant agreement is obtained from our model as compared with the data of Mulder and Louw at two temperatures for both product formation and anisole decay. The model also accurately predicts the results of Mackie et al. on anisole pyrolysis and oxidation. The second exciting development is that the first draft of a dioxin formation mechanism is complete and in validation; though, it is too early to show data trends with confidence. At levels of precursors around 1 ppm, however, the mechanism predicts levels of PCDD/Fs several orders of magnitude lower. In this mechanism, we have a number of routes to formation; however, we need additional routes to destruction.

Our ClHC mechanisms have been used by the MIT Group (A. Sarofim, J. Longwell) in a collaborative effort to model stable species measured in an MIT bench scale turbulent combustor. This work has addressed both the ClHC inhibition issue as well as the effects of incomplete micromixing on PIC formation.

COLLABORATION WITH EPA RESEARCH TRIANGLE PARK GROUP

During the current reporting period, our collaboration with the EPA-RTP combustion group began with an on-site meeting. An overall strategy was developed and experimental and modeling plans were made. The emphasis of the research will be placed on the afterburner (secondary combustion chamber) of the RTP incinerator simulator.

Phase I will employ a Pyretron burner with downstream choke in the afterburner, while phase II will use a Variable Swirl burner and no choke. Each phase will begin with cold flow velocity pitot tube measurements. Then SO2 tracer studies will be performed under various combustion conditions; e.g., with and without flow from the primary chamber (kiln). These tracer data will be forwarded to NJIT for residence time distribution analysis. A reactor model based on a complex combination of ideal reactors [perfectly stirred reactor (PSR) and plug flow reactor (PFR)] has been created for this purpose. Ideally, the afterburner would behave as a PSR followed by a PFR. The departure from this ideal will be determined from the tracer work. This model is currently operational. RTP reports that cold flow and tracer studies for Phase I will begin early in the 4th quarter of this year.

Phase III involves an extensive series of afterburner combustion tests. Baseline runs will involve a natural gas fuel. Then chlorinated dopants will be added (CH2Cl2, CHCl3, and monochlorobenzene). Continuous emission monitoring will be performed (CO, CO2, O2, etc.) as well as other analyses. Staged combustion experiments are also planned in which fuel-rich combustion is maintained in the first zone, with added air/fuel/steam injected into the second stage. Species and temperature data will be forwarded to NJIT for detailed modeling using a generalized reactor engineering model developed expressly to model the EPA afterburner. This model employs the CHEMKIN package and will utilize the NJIT mechanisms discussed above. At a later date, a linear eddy turbulent mixing model developed at MIT will be used in modeling the afterburner.

RELEASE OF CHLORINATED ORGANIC COMPOUNDS FROM A CONTAMINATED ESTUARINE SEDIMENT

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INTRODUCTION

In spite of major efforts to protect the nation's water bodies from toxic chemicals, contamination of aquatic ecosystems still persists. Contaminated bottom sediments, previously thought of as natural sinks for contaminants in aquatic ecosystems, are now viewed as a major source of contamination. Due to the persistence of the sediment contaminants, emphasis has recently been placed on the fate and transport of in-place pollutants. Although research on contaminated sediments has intensified in the last decade, we still lack fundamental knowledge of the processes and process interactions that govern the partitioning and transformation of sediment-bound toxic chemicals.

Recent investigations and monitoring of the Bayou d' Inde, a tributary of the Calcasieu River in Southwestern Louisiana, have shown that high-molecular-weight chlorinated organic compounds (benzenes and butadiene) and metals (chromium, copper, lead, mercury, nickel) persist in the sediments. In addition, seafood species were found to be contaminated with hexachlorobenzene and hexachloro-1,3-butadiene and the sediments produced chronic toxicity to aquatic life (1). A research project was initiated to investigate the mechanisms and transformations related to the fate of the halogenated organic compounds found in the sediments of Bayou d' Inde. This report deals with desorption kinetics and the equilibria of sediment-bound chlorinated organic compounds.

METHODOLOGY

Two sampling stations were located in the Bayou d' Inde, one in an industrial canal connected to the Bayou d' Inde whereas a fourth station was located in the Calcasieu River above a salt water barrier. Sediment and water samples were collected in April 1993 and analyzed for pH, alkalinity, major anions (Cl^-, SO_4^-, NO_3^-, PO_4^-), volatile and dissolved solids, volatile and extractable chlorinated organic compounds, total organic carbon, and dissolved organic and inorganic carbon. In situ, aqueous parameters -- such as pH, temperature, conductivity, salinity, and dissolved oxygen -- were also measured at a depth of 1 m.

Standard methodologies were used for most of the analyses (2, 3, 4, 5). Sediment samples were first extracted using the Soxhlet technique in a 1:1 (v/v) acetone:hexane solvent mixture, the extract was then concentrated and the solvent was changed to isooctane. The sediment extract was then analyzed by gas chromatography (electron capture detector). Liquid/liquid extraction with isooctane was used to concentrate the aqueous contaminants. Tribromobenzene was used as an internal standard.

Desorption experiments were performed in batch reactors. Sediment samples were placed in a series of Teflon centrifuge tubes and then diluted with deionized water allowing for a headspace. The final solids concentration was ca. 3% (w/v). Sodium azide was added to each tube (2 g/L final concentration). The tubes were then capped and continuously rotated on a mechanical tumbler (1 rpm). Three tubes at a time were periodically removed and centrifuged at 12,000 rpm for 25 min. The supernatant was liquid/liquid extracted and then analyzed by gas

chromatography. After centrifugation, Soxhlet extraction of the sediment pellet was periodically performed for mass balance calculations. Similar batch desorption experiments were also performed using 2-L wide-mouth glass jars.

Batch equilibrium desorption experiments were performed as follows. Differing masses of sediment were added to twelve 160-ml serum bottles, then diluted with deionized water (sodium azide included) allowing for headspace. Triplicate serum bottles were prepared with the following solids concentrations: 0.6, 1.5, 2.8 and 5.7% (w/v). The serum bottles were placed on a mechanical tumbler, and rotated continuously at 1 rpm. After 40 days, the serum bottles were removed, their contents placed in Teflon tubes and centrifuged at 12,000 rpm for 25 min. The supernatant was removed, liquid/liquid extracted and then analyzed by gas chromatography. The sediment pellet of one replicate from each solids concentration was Soxhlet extracted and the extract was then analyzed by gas chromatography.

Finally, a differential reactor (mini-column) was set-up to simulate continuous-flow conditions. Deionized water containing 2 g/L of sodium azide was pumped at a flow rate of 3.1 mL/d through a stainless steel column containing 0.4414 g of sediment. The eluent was directly collected in a 20-mL glass syringe and periodically analyzed by liquid/liquid extraction and gas chromatography.

RESULTS

System Characterization

The in-situ measurements resulted in the following ranges: pH, 6 to 7.3; temperature, 19 to 29°C; conductivity, 40 to 4,630 μmho/cm; salinity, 0 to 2.5‰; dissolved oxygen, 5.7 to 5.9 mg/L. Analyses of water samples performed in the laboratory resulted in the following parameter value ranges: pH, 6.6 to 7.6; conductivity, 44 to 4,150 μmho/cm; total suspended solids, 6 to 20 mg/L; dissolved organic carbon, 10.6 to 12.7 mg/L; sulfate, 4 to 76 mg/L; chloride, 3 to 1220 mg/L; hexachloro-1,3-butadiene (HCBD), 0.4 to 2 μg/L; hexachlorobenzene (HCB), 1 to 2 μg/L. Parameter values for the sediments ranged as follows: pH, 6.6 to 7.4; total organic carbon, 2 to 4.8% dry mass; total sulfide, 0.2 to 1.6 mg/g dry mass. The distribution of sediment particles was as follows: sand, 66 to 71%; silt, 12 to 19%; clay, 4 to 5%; and colloids, 9 to 12%. The following chlorinated organic compounds were identified in sediment extracts from samples collected in the Bayou d' Inde and the industrial canal (mg/kg dry weight basis): dichlorobenzenes, 3.9; trichlorobenzenes, 2.6 to 27.5; tetrachlorobenzenes, 0.5 to 10.4; pentachlorobenzene (PeCB), 3.4 to 20.1; HCB, 8.9 to 123; and HCBD, 5.6 to 36. Therefore, HCBD and chlorobenzenes with high chlorine content are the predominant sediment contaminants.

Release of Sediment-Bound Contaminants

Five chlorinated organic compounds were consistently found in the aqueous phase during the desorption experiments: HCBD, HCB, PeCB, 1,2,4,5-tetrachlorobenzene (1245-TeCB), and 1,2,4-trichlorobenzene (124-TrCB). The desorption pattern of the chlorinated organic compounds was biphasic: a fast first release, followed by a much slower rate of release (Fig. 1). With the exception of 124-TrCB which resulted in ca. 3% desorption within 62 d, the other four contaminants showed less than 0.5% desorption, based on the time zero contaminant content of the solid phase. The carbon attributed to the chlorinated organic contaminants accounted for less than 0.03% of the total DOC released within 62 d of incubation. The rate and extent of contaminant desorption from sediment samples taken from different stations was inversely correlated to the organic carbon content of the samples.

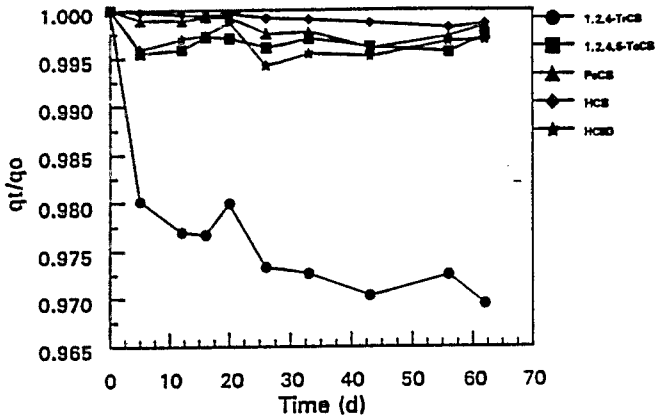

Figure 1. Desorption pattern of sediment-bound chlorinated organic compounds.

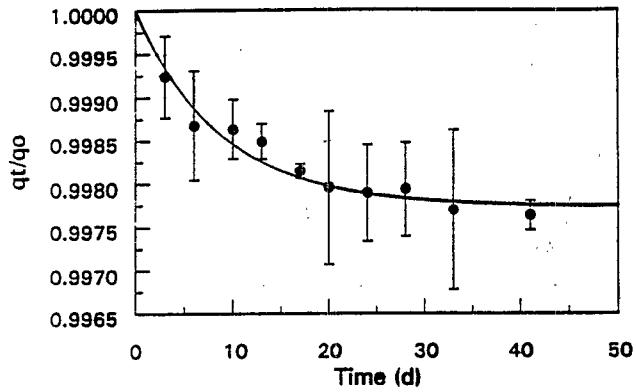

Figure 2. Desorption pattern of HCB (data points and 95% confidence intervals) and simulation based on the two-site model (continuous line).

The desorption isotherms for all five contaminants fitted the linear model with a desorption-resistant contaminant solid-phase concentration (q_r, μg/kg), as follows: $q = q_r + K_f C_e$ where: q = total solid-phase contaminant concentration, μg/kg; K_f = partition coefficient, ml/g; and C_e = liquid-phase contaminant concentration, μg/ml. The partition coefficients (K_f) pertain only to the contaminant portion that can freely achieve equilibrium. Based on the two-site model, K_f refers to the equilibrium achieved at the fast sites. The overall partition coefficient is expressed as follows: $K_p = K_f + K_s$, where K_s refers to the partition coefficient describing the desorption equilibrium at the slow sites. Based on the experimental data, a fit of the two-site model resulted in the following ranges for the K_p values (in ml/g): 124-TrCb, 276 to 410; 1245-TeCB, 2610 to 5600; PeCB, 3330 to 3930; HCB, 5190 to 5750; and HCBD, 2210 to 2520. Figure 2 shows the two-site model fit to the desorption data of HCB. When the partition coefficients were normalized to the organic carbon content of the samples, the following partition coefficient values resulted (log K_{oc}): 124-TrCb, 3.76 to 3.93; 1245-TeCB, 4.73 to 5.07; PeCB, 4.84 to 4.91; HCB, 5.03 to 5.08; and HCBD, 4.66 to 4.72. These values compare favorably with literature reported K_{oc} values (6). The first-order constant describing the microscopic net desorption rate from the slow sites was estimated and varied as follows (in d^{-1}): 124-TrCB, 0.061 to 0.080; 1245-TeCB, 0.013 to 0.018; PeCB, 0.001 to 0.008; HCB, 0.002 to 0.008; and HCBD, 0.0129 to 0.0135.

When the continuous-flow mini-column was used, the extent of contaminant desorption was greater than that previously attained by the batch desorption experiments. Because of the high operating pressure (ca. 4,500 psig), it is likely that the eluent was in contact with sites that were more secluded under the conditions of all previous batch experiments. After about 3600 pore volumes of deionized water had passed through the sediment sample (in about 57 days), the highest extent of desorption was observed for HCBD (ca. 14%). The extent of desorption was higher for the less hydrophobic contaminants (Fig. 3). The fraction of the solid-phase contaminant which desorbed was linearly correlated with the logK_{oc} of the contaminants (Fig. 4). The values of the first-order desorption constant from the slow sites were estimated as follows (in d^{-1}): PeCB, 0.0017; HCB, 0.000013; and HCBD, 0.0485.

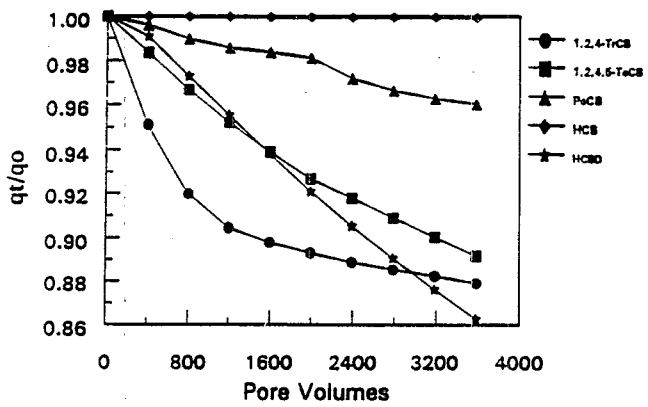

Figure 3. Continuous-flow desorption of sediment-bound chlorinated organic compounds (mini-column).

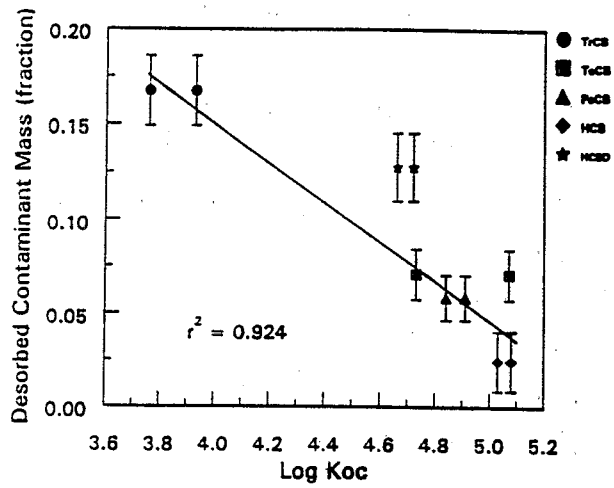

Figure 4. Correlation between extent of continuous-flow desorption (mini-column) and K_{oc} of sediment-bound chlorinated organic contaminants (HCBD was not included in the linear regression analysis).

CONCLUSIONS

In a period of several weeks, 3% or less of the sediment-bound contaminants desorbed under batch conditions. Continuous-flow simulation increased the overall extent of desorption, but it did not exceeded 15% for a similar period of time. The desorption of the sediment contaminants followed a biphasic pattern, which was described by a two-site, first-order linear model. A very small fraction of the contaminant mass is associated with fast desorbing sites, most of the contaminant mass undergoes a very slow desorption. Resistance to desorption is primarily due to the high hydrophobicity of the contaminants and the relatively high organic carbon content of the sediments.

REFERENCES

1. Cunningham P. et al. Toxics Study of the Lower Calcasieu River. PB90 226150/AS, National Technical Information Service, Springfield, VA, 1990.

2. American Public Health Association. Standard Methods for the Examination of Water and Wastewater, 17th ed., APHA-AWWA-WPCF, Washington, DC, 1989.

3. Page, A. L. (ed.). Methods of Soil Analysis - Part 2: Chemical and Microbiological Properties, 2nd ed., American Society of Agronomy, Inc., and Soil Science Society of America, Inc., Madison, WI, 1982.

4. U. S. Environmental Protection Agency. Test Methods for Evaluating Solid Waste. SW-846, 3rd ed., EPA/OSWER, Washington, DC., 1986.

5. American Society for Testing and Materials. Annual Book of ASTM Standards. Philadelphia, PA., 1990.

6. Gess, P.L. Release of Chlorinated Organic Compounds from a Contaminated Estuarine Sediment. MS Thesis, Georgia Institute of Technology, 1994.

FLUME STUDIES ON THE DETACHMENT OF KAOLINITE CLAY AND ASSOCIATED CONTAMINANTS FROM A COARSE SEDIMENT

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INTRODUCTION

Waste discharges from point sources and nonpoint pollution originating from agricultural and urban runoff have led to the storage of pollutants such as pesticides and heavy metals within the sediment bed of many water bodies. These pollutants are often adsorbed to clay particles in fine sediments which also provide cohesiveness of the sediment bed. The prediction of erosion or resuspension of these clay particles and associated contaminants at the sediment-water interface in rivers, lakes, and estuaries is vital to the hazard assessment and remediation of contaminated aquatic sediments.

Previous relationships developed for predicting erosion and resuspension of fine sediments are highly empirical. They depend on empirical coefficients which vary with the particular sediment-water system of interest, and which are often estimated by ad hoc laboratory procedures that do not necessarily reproduce the hydrodynamic and physicochemical processes occurring at the sediment-water interface. Most numerical models of the fate and transport of fine sediments and associated contaminants depend on these highly tenuous empirical relationships for the erosion and resuspension process.

Sediment pick-up functions for noncohesive sediments have long been formulated as a function of the excess shear stress with respect to a critical shear stress which is required for initiation of motion (1). This approach has enjoyed considerable success for noncohesive sediments because the primary force resisting initiation of motion is the submerged weight of individual sediment grains so that the critical shear stress depends primarily on grain size. In fine sediments with a significant clay fraction, however, interparticle physicochemical forces which cause cohesion also resist initiation of motion, and these forces have proved much more difficult to quantify. These cohesive sediment forces depend on many factors, which include amount and type of clay mineral, degree of consolidation, type and concentration of ions in the water, and the presence of natural organic matter (2).

Other mechanisms besides erosion and resuspension exist for contaminant transfer at the sediment-water interface including such processes as bioturbation and diffusion. However, Sheng (3) estimates that sediment resuspension fluxes associated with episodic or diurnal events can be 10 to 100 times the diffusive flux. On the other hand, estimates of erosion or resuspension by empirical formulas differ by as much as two orders of magnitude (3).

Recent advances in estimating the fundamental forces required for detachment of colloidal particles from larger sediment grains offer a new approach for quantifying the forces resisting erosion/resuspension of cohesive sediments (4). Theoretical expressions have been developed to estimate the magnitude of interparticle forces, including electrostatic and van der Waals forces, which control particle detachment (4). Ongoing research sponsored by the EPA Hazardous Substance Research Center/South and Southwest has the goal of applying calculations of interparticle forces to the problem of estimating erosion and resuspension rates of cohesive bottom sediments and associated contaminants as a function of ionic strength and concentration of natural organic matter. Experimental studies are being conducted in a laboratory flume in which the flow field is similar to the actual shear flow experienced by field sediments. The results of these interparticle force calculations and experimental flume studies are applicable to numerical models used in the evaluation of the transport of contaminated bottom sediments in lakes and rivers due to natural erosion and resuspension, resuspension due to dredging activities, and erosion of contaminated particles as affected by salinity changes in estuaries.

METHODOLOGY

The initial experimental approach to the problem has been to attach kaolinite clay particles to a fine gravel which forms the movable but stable bed of a recirculating, tilting flume, and to measure the detachment of the clay particles as a function of applied shear stress. A definition sketch of the flume is shown in Figure 1. It is approximately 6 m long by 38 cm wide. The flow rate is measured by a calibrated bend meter, and uniform flow is obtained by adjusting the tailgate. Extensive tests were conducted in the flume to establish depth-discharge relationships for uniform, subcritical flow at slopes of 0.002, 0.003, and 0.004 with channel aspect ratios (width/depth) ranging from 5 to 10. In addition, velocity profiles were measured using a Pitot tube connected to a differential pressure transducer, amplifier, and voltmeter which were controlled by a microcomputer.

The measurement of centerline velocity profiles showed that the boundary layer was fully developed at the flume test section. Measured centerline velocity profiles were used to predict shear stress in a central core of the flow at the test section by measuring the slope of the semilogarithmic velocity profile near the bed. The shear stresses measured from the velocity profiles are compared with those obtained from the uniform flow formula in Figure 2.

Several series of particle erosion tests in the flume have been conducted. In a sample tray placed at the centerline of the test section of the flume, the large, noncohesive sediment grains (fine gravel) comprising the bed are coated with a kaolinite clay suspension. The fine gravel has a mean grain size of 3.3 mm, while the kaolinite clay has a mean particle size of approximately 1.5 μm. Uniform flow conditions are established, and the plume of eroded/detached clay particles is measured as a function of time using a Chemtrac continuous particle monitor and a Hach turbidimeter. The particle monitor measures fluctuations in light intensity transmitted through a sample stream flowing through a transparent tube. Continuous samples are also collected which can be analyzed for particle number concentration and size distribution (0.5 to 150 μm) with a Brinkmann particle analyzer. A separate sample stream is collected for filtration analysis of total mass eroded.

RESULTS

Typical results for a series of flume experiments are shown in Figures 3 and 4. Figure 3 shows an increase in total mass of kaolinite clay eroded with increasing bed shear stress. In this series of experiments, the shear stress varied from 0.9 to 1.6 N/m^2. The total mass eroded in Figure 3 was determined from three separate measurements which included filtered mass, particle number concentration from the Brinkmann particle analyzer, and the particle monitor output. Although it appears from these results that a critical shear stress exists for zero mass eroded, additional experiments are needed to pinpoint its value.

In Figure 4, the cumulative mass erosion curves as determined from the particle number concentration data are shown as a function of time for the conditions of minimum and maximum bed shear stress in Figure 3. The slope of the erosion curves indicates the erosion or detachment rate per unit surface area of the contaminated bed sample. The erosion rate decreases with time as the total mass eroded is approached. Both the total mass eroded and the initial erosion rate increase with increasing bed shear stress. Additional flume experiments are planned to determine the effects of ionic strength of the eroding water and adsorbed natural organic matter on the erosion rate of kaolinite clay as well as field samples of contaminated sediment. These erosion rates will be parameterized based on calculations of the microscopic forces which are required to detach colloidal-sized particles from a sediment bed (5).

CONCLUSIONS

Erosion or detachment of kaolinite clay particles from much larger, noncohesive sediment grains depends on excess shear stress with respect to a critical shear stress. Both the total mass eroded and the initial time rate of erosion increase with increasing shear stress. Future experiments should be directed toward characterizing the erosion and transport of cohesive sediments in terms of the microscopic interparticle forces which vary with ionic strength, type of clay, and concentration of natural organic matter.

REFERENCES

1. Vanoni, V. (ed.). Sedimentation Engineering. ASCE Manual No. 54. American Society of Civil Engineers, New York, 1977.

2. Mehta, A.J., Hayter, E.J., Parker, W.G., Krone, R.B., and Teeter, A.M. Cohesive Sediment Transport, I: Process Description. ASCE Journal of Hydraulic Engineering. 115 (8): 1076-1093, 1989.

3. Sheng, Y.P. Task Committee on Transport Processes at the Interface of Water Column and Bottom Sediment. In: Proceedings of the 1990 National Conference on Hydraulic Engineering, ASCE, New York, 1990. p. 47.

4. Amirtharajah, A. and Raveendran, P. Detachment of Colloids from Sediments and Sand Grains. Colloids and Surfaces. 73: 211-227, 1993.

5. Raveendran, P. Mechanisms of Particle Detachment During Filter Backwashing. Ph.D. Thesis presented to the School of Civil Engineering, Georgia Institute of Technology, Atlanta, Georgia, November, 1993.

FOR MORE INFORMATION

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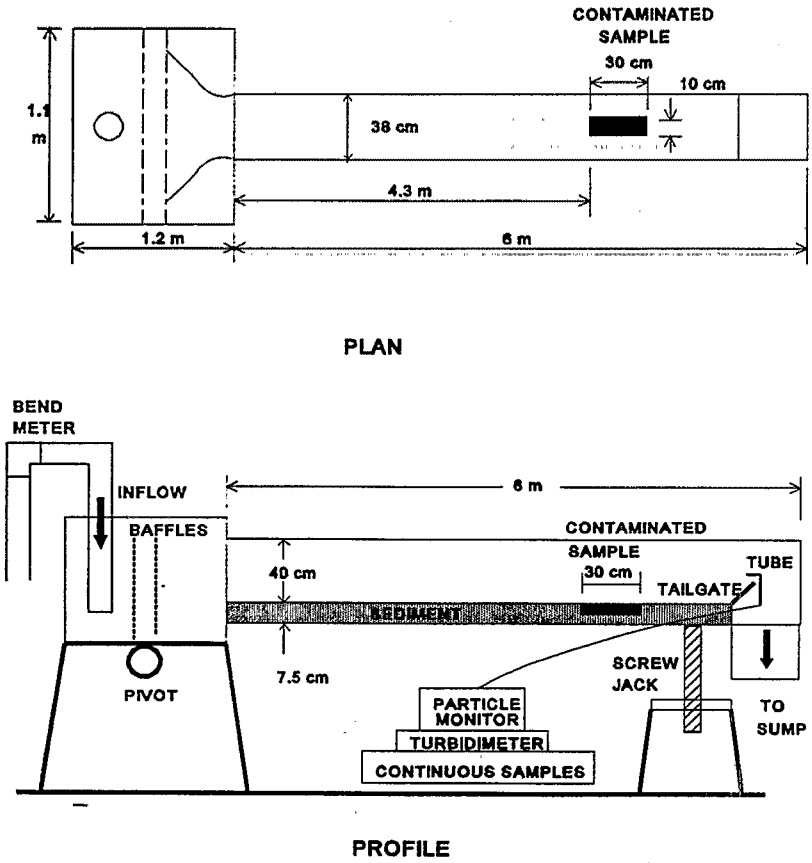

Figure 1. Plan and Profile of Flume.

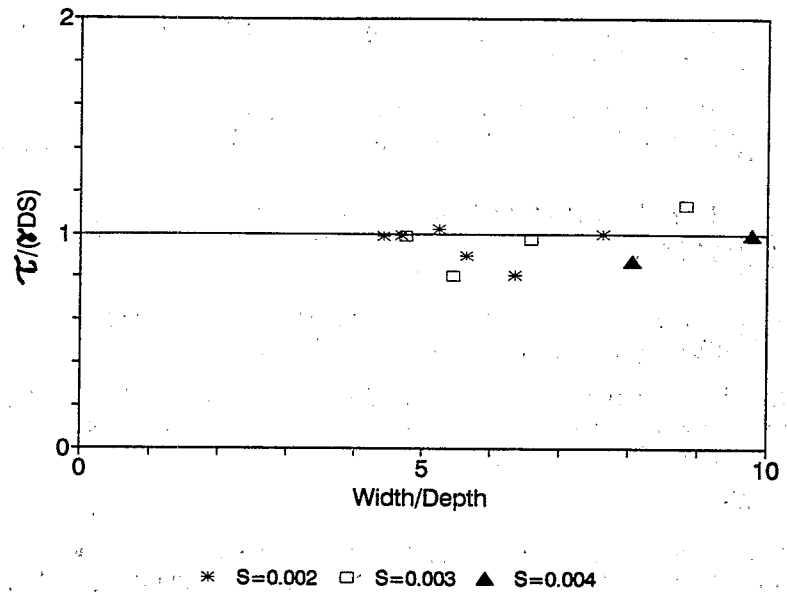

Figure 2. Comparison of Shear Stress, τ, Determined From Velocity Profiles and Uniform Flow Formula, γDS (γ=specific weight of water, D=depth of flow, S=bed slope).

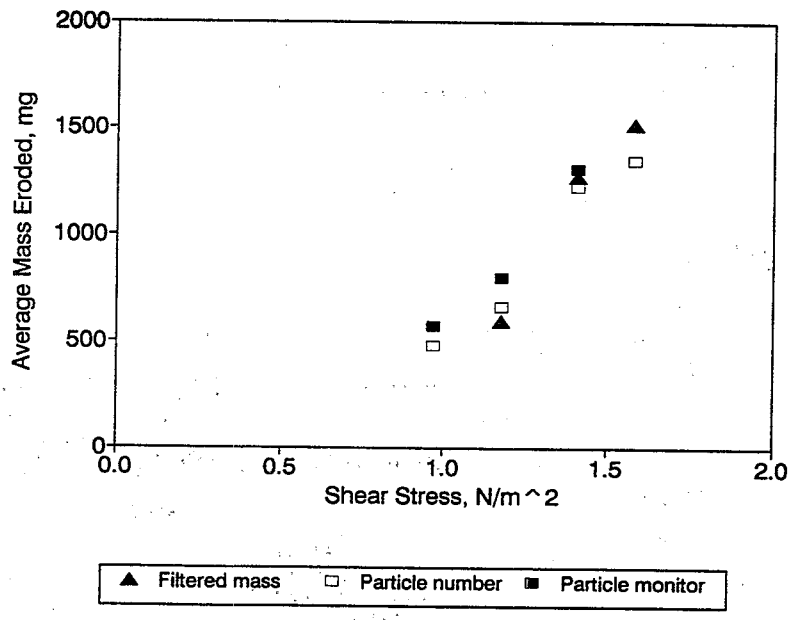

Figure 3. Total Mass of Kaolinite Clay Eroded From Sample Tray.

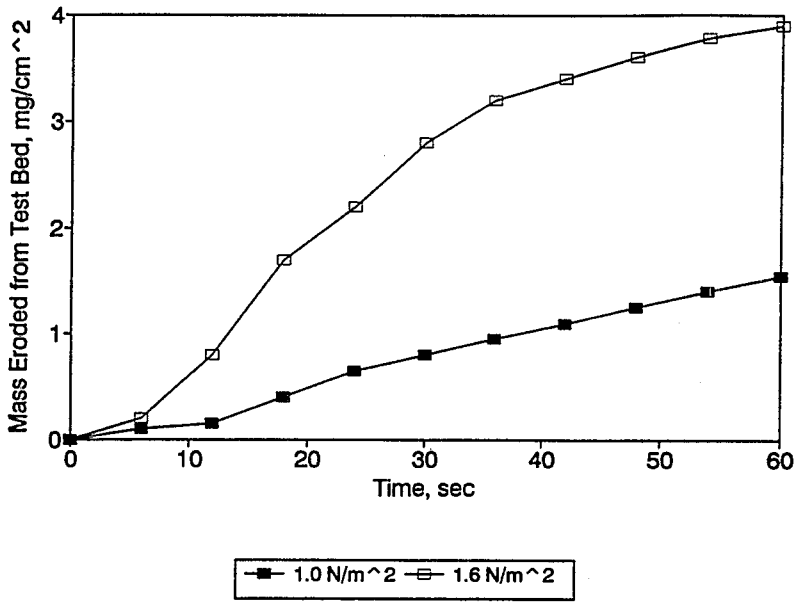

Figure 4. Cumulative Mass of Eroded Kaolinite Clay as a Function of Time for Shear Stresses of 1.0 and 1.6 N/m^2.

THE U.S. EPA INCINERATION RESEARCH FACILITY

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The U.S. EPA's Incineration Research Facility (IRF) located in Jefferson, Arkansas, houses bench-scale and pilot-scale incinerators including a rotary kiln system (RKS) and a thermal treatability unit (TTU). The RKS consists of a 2.0 MMBTU/hr rotary kiln primary chamber, a gas-fired 1.5 MMBTU/hr afterburner, and primary and secondary air pollution control systems (APCS). It is capable of incinerating solid and liquid wastes. In 1993 the existing APCS was enhanced by the installation of a flue gas reheater and fabric filter baghouse. The waste handling capabilities of the IRF were also improved by the addition of a scrubber/waste liquid containment tank-system with a total storage capacity of 18000 gallons. The TTU is a small commercial pathological waste incinerator converted to allow thermal treatment of liquid and solid wastes in a semi-batch continuous mode. Quartz trays (8-in x 10-in x 2-in) containing up to 2 lb of test materials each can be subjected to thermal treatment conditions for 20 min to 2 hr.

Three major test programs were completed in 1993 at the IRF using the RKS. The first was in support of the Office of Emergency and Remedial Response's (OERR) Superfund site remediation program, and was an evaluation of the decontamination of soils contaminated with organic constituents in the rotary kiln operating at low to moderate temperatures associated with thermal desorption. The second was a major third-party test program in which a series of tests with simulated low level mixed waste were conducted for the Westinghouse Savannah River Company, the operating contractor for the Department of Energy Savannah River Plant and Savannah River Technical Center. The third test program of 1993 was in support of EPA Region III, and the U.S. Army Corp of Engineers to evaluate the incinerability of contaminated soil and a fluff waste from the M.W. Manufacturing Superfund site in Pennsylvania.

A current test program is a demonstration which is, the incineration of the Russian Federation's ballistic missile propellant components comprised of unsymmetrical dimethyl hydrazine (UDMH) as the fuel, and dinitrogen tetroxide as the oxidizer (N_2O_4). This program is supported by the Defense Nuclear Agency as part of the Strategic Arms Reduction Treaty (START) negotiations, and will demonstrate that incineration of UDMH and N_2O_4 can be achieved to levels acceptable to both Russian and U.S. environmental regulations. An ongoing test program using the TTU was initiated in FY93 to evaluate the effectiveness of silica/alumina/clay based additives as sorbents for metal capture.

Results from the previous year's tests and current year activities will be highlighted in the poster presentation. For more information contact R. C. Thurnau, the EPA project officer at the above address.

FOUR YEAR STUDY OF ASBESTOS IN NEW JERSEY PUBLIC SCHOOLS

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Introduction

The U.S. Environmental Protection Agency (EPA) recommends a pro-active, in-place management program whenever asbestos-containing material is present in buildings. Asbestos removal is required only when necessary to prevent significant public exposure to airborne asbestos during building demolition or renovation activities. The ultimate goal of every asbestos abatement project is to eliminate, or reduce to the extent possible, the actual or potential hazard airborne asbestos may present to building occupants. If all safeguards are not properly applied, asbestos removals may actually elevate airborne levels of asbestos in a building.

In 1988, EPA-RREL and NJDOH-EHS conducted a study to document Asbestos Hazard Emergency Response Act (AHERA) air-sampling practices during final clearance and to measure final clearance levels of airborne asbestos at 20 projects involving removal of asbestos-containing material (ACM) in 17 New Jersey schools. In 1990, EPA/NJDOH conducted a study at the same 17 schools to measure airborne asbestos levels 2 years after the abatements in 1988. Although the 1990 study provided data regarding the residual levels of asbestos 2 years after abatement, the extent to which these data represented conditions of actual occupancy remained uncertain. In 1991, EPA/NJDOH measured airborne asbestos levels under occupied conditions at the 17 schools 3 years after abatement. In 1992, EPA/NJDOH conducted a final study at the 17 schools to measure airborne asbestos levels under actual occupied conditions 4 years after abatement.

Conclusions

1) Overall, when all of the 20 sites were considered collectively, there was no apparent trend toward progressively increasing airborne asbestos concentrations 2 to 4 years after the 1988 abatements.

2) Response actions conducted by the schools in 1991 and 1992 demonstrated that elevated airborne asbestos levels can be reduced to acceptable levels (i.e., <0.02 s/cm^3).

3) Asbestos-containing debris from the 1988 abatement and from postabatement operations and maintenance (O&M) activities may have contributed to the elevated airborne asbestos levels (>0.02 s/cm^3) present in 1991 and/or 1992 at nine sites.

4) Errors in the Asbestos Management Plans relating to material identification or material location were documented at 13 of the 17 schools.

5) When the AHERA Z-test is used to clear an abatement project, it is generally more appropriate to utilize the outdoor samples as the reference point than the perimeter samples collected inside the building.

UPDATE OF THE EPA DEVELOPED FULL SCALE DEBRIS WASHING SYSTEM

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The automated, transportable (mounted on three semi-trailers), self-contained debris washing system (DWS) developed by IT Corporation for EPA's Risk Reduction Engineering Laboratory is ready for deployment to a hazardous waste site for an initial demonstration of the new system. Depending upon the debris characteristics, the DWS can decontaminate between 50 to 120 tons per day.

Experience gained under actual field conditions when the pilot-scale DWS was demonstrated under the Superfund Innovative Technology Evaluation (SITE) Program confirmed that the DWS technology had definite promise for addressing decontamination of metallic debris at hazardous waste sites. Results of the pilot-scale demonstration indicated areas where improvements could be made in the system and led to the design and development of the full-scale unit.

The full-scale system includes a 12-ft long by 7-ft wide by 8-ft deep cleaning chamber, where the wash, spray and rinse process steps occur. Unit operations require loading a heavy-duty basket with approximately 2 tons of crane-lifted metallic debris, positioned on cradles, in the cleaning chamber. The hydraulically-operated cover of the cleaning chamber is closed and 2000 gallons of 160° F detergent solution is introduced, the basket is rotated and the turbulent wash cycle is started. After the wash cycle, the detergent solution is pumped back into the detergent holding tank and the spray cycle starts. During this cycle detergent solution is delivered at 500 gal/min through spray nozzles located inside the basket. A portion of the cleaning solution is cycled through a closed-loop oil-water separator system, and then recycled back into the detergent holding tank.

The rinse cycle is then instituted where clean water is applied through the spray nozzles to remove residual-contaminated liquid from the debris surfaces. Time required for each cycle varies depending on type of site, contamination, debris and other variables.

For more information: Michael Taylor or Majid Dosani, IT Corporation, 11499 Chester Road, Cincinnati, OH 45246, (513) 782-4700.

AN EVALUATION OF DRINKING WATER SAMPLES PREPARED USING ULTRAFILTRATION AND UV-TiO_2 TECHNOLOGIES

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In the United States approximately 25 million people receive their drinking water from small systems (serving fewer than 3,300 people). These systems are the most frequent violators of federal drinking water regulations. As the number of regulations increase, compliance will become even more difficult for small systems to achieve. Package plants, water treatment units assembled in a factory that arrive at a site virtually ready to use, are currently being evaluated as feasible treatment options for small systems.

In the present study, drinking water was prepared using a combination of ultrafiltration and photocatalysis, both applicable to use in package plants. Previous results indicate that ultrafiltration followed by chlorination removed microbiological contaminants. However, based on the levels of total organic halide (TOX) and mutagenicity observed, the levels of disinfection by-products (DBP) in the finished water appeared to be essentially the same as in chlorinated raw water. Consequently photocatalysis, using UV light and titanium dioxide (TiO_2), was employed. This process has been shown to cause the oxidative destruction of many organic compounds.

At the Test and Evaluation Facility, Mill Creek water was treated using ultrafiltration then recirculated through the UV-TiO_2 unit until a 10% reduction in total organic carbon (TOC) was produced. A portion of the water treated by ultrafiltration and UV-TiO_2 was subsequently chlorinated. Samples of raw water, raw water + chlorine (Cl_2), and ultrafiltered water with and without Cl_2 were also prepared. TOC, TOX, and microbiological contaminants were determined for each sample. Concentrates of the organic compounds in each water sample were prepared by XAD resin chromatography. These concentrates were assayed for mutagenicity in the Ames assay and used for the identification of DBP by gas chromatography/mass spectrometry.
(This abstract does not reflect EPA policy).

For more information contact Kathleen S. Patterson, USEPA, RREL, DWRD, SFEB, 26 W. M. L. King Drive, Cincinnati, Ohio 45268, 513/569-7947.

RREL SITE REMEDIATION TECHNICAL SUPPORT PROGRAM

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The Risk Reduction Engineering Laboratory provides a variety of technical support to Regional Remedial Project Managers and other site remediation managers and contractors. This poster will highlight some of these support activities in the areas of site-specific assistance and technology transfer, including:

- treatability study assistance
- site-type specific remediation guidance documents
- technology specific documents
- computerized databases

Forms for ordering technology transfer documents will be available.

For more information: Benjamin L. Blaney.

THE ENVIRONMENTAL PROTECTION AGENCY'S INNOVATIVE TECHNOLOGY PROGRAM

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President Clinton announced a proposal in the State of the Union speech in February 1993, aimed at protecting the environment while strengthening America's industrial base. The **Environmental Technology Initiative (ETI)**, which began this year, is a long term program that will allocate $1.85 billion dollars over the next nine years to develop more advanced process changes and treatment and control technologies that yield environmental benefits and increase economic growth. Although the ETI is a complete environmental technology program that considers all the factors necessary to commercialize and sell innovative technologies, this poster session focuses on the Risk Reduction Engineering Laboratory's research, development, and demonstration projects.

EPA's **Innovative Technology Council (ITC)** is an internal Agency advisory and advocacy group dedicated to fostering the development, commercialization, and use of innovative technologies. The ITC selected four areas to fund projects in 1994. EPA has solicited partners from outside the Agency who will leverage funding and provide expertise in the following areas.

1. Clean Technology for Small Businesses

This area attempts to bring the benefits of pollution prevention to small companies by having EPA and selected partners act as a convener and educator. Projects fall into three categories: technical assistance; joint research with industry; and research on safer chemicals, products, materials, and systems.

2. Improving Global Competitiveness of U.S. Environmental Technologies

The U.S. Technology for International Environmental Solutions (U.S. TIES) initiative promotes technical assistance, training and information dissemination, in-country demonstrations, evaluation and testing, feasibility studies, market and needs assessments, and international standards development.

3. Innovative Technologies Development

The Innovative Technologies Development initiative is directed toward developing, testing, evaluating, and bringing into the marketplace technologies that first, address the most critical needs of EPA programs, and second, exhibit the greatest potential for important technological breakthroughs.

4. Gaps, Barriers, and Incentives

This initiative is designed to explore the reasons why innovative technologies are not pursued by investors, venture capitalists, and the regulated industry purchasers. This area intends to identify the barriers, changes, and incentives that will promote the commercialization and sale of innovative technologies.

The Risk Reduction Engineering Laboratory's innovative technology projects and partners will be identified in handout material. In addition, information and Agency contacts will be available for the complete ETI program.

For information on the Risk Reduction Engineering Laboratory's programs, contact:

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For information on the ETI (EPA's total innovative technology program), contact:

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202-260-3861 (FAX)

For information on the ITC (EPA's innovative technology strategy), contact:

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EVALUATION OF IN-VESSEL COMPOSTER DESIGNS FOR HAZARDOUS WASTE TREATMENT

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ABSTRACT

Composting techniques have been successful in treating municipal solid waste. Recent efforts by the U.S. Army to treat soils contaminated with munition chemicals have identified a new application of composting to the treatment of solid materials contaminated with hazardous waste. The munition composting has been conducted in field situations using open composting conditions. The mass balance of the munition chemicals in such application sis not easy to track. Our research is designed to assess the potential of composting as applied to hazardous waste constituents. We have conducted a developmental program to evaluate the performance of several in-vessel composting bioreactors to ensure optimal control of the composting process and gain information about the mass balance of the targeted contaminant. As such the reactors are designed as diagnostic tools to evaluate composting conditions for specific waste materials in contaminated solid matrices. These reactor systems are designed to mimic composting conditions with instrumented control of process factors. The reactor designs will be discussed with initial performance data.

ACOUSTIC LOCATION OF LEAKS IN PRESSURIZED UNDERGROUND PETROLEUM PIPELINES

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ABSTRACT

Millions of underground storage tanks (USTs) are used to store petroleum and other chemicals. The pressurized underground pipelines associated with USTs containing petroleum motor fuels are typically 2 in. in diameter and 50 to 200 ft in length. These pipelines typically operate at pressures of 20 to 30 psi. Longer lines, with diameters up to 4 in., are found in some high-volume facilities. When a leak is detected, the first step in the remediation process is to find its location. Passive-acoustic measurements, combined with advanced signal-processing techniques, provide a nondestructive method of leak location that is accurate and relatively simple, and that can be applied to a wide variety of pipelines and pipeline products.

Experiments were conducted at the UST Test Apparatus Pipeline in which three acoustic sensors separated by a maximum distance of 38.1 m (125 ft) were used to monitor signals produced by 11.4, 5.7, and 3.8 L/h (3.0, 1.5, and 1.0 gal\h) leaks in the wall of a 5 cm (2 in.) diameter pressurized petroleum pipeline. The line pressures and hole diameters used in the experiments ranged from 69 to 138 kpa (10 to 20 psi) and 0.4 to 0.7 mm (0.01 to .03 in.), respectively. Application of a leak location algorithm based upon the technique of coherence function analysis resulted in mean difference between predicted and actual leak locations of approximately 10 cm.

Spectra computed from leak-on and leak-off time series indicate that the majority of acoustic energy received in the far field of the leak is concentrated in a frequency band from 1 to 4 kHz. The strength of the signal within this band was found to be proportional to the leak flow rate and line pressure. Energy propagation from leak to sensor was observed via three types of wave motion: longitudinal waves in the product, and longitudinal and transverse waves in the steel. The similarity between the measured wave speed and the nominal speed of sound in gasoline suggests that longitudinal waves in the product dominate the spectrum of received acoustic energy. The effects of multiple-mode wave propagation and the reflection of acoustic signals within the pipeline were observed as non-random fluctuations in the measured phase difference between sensor pairs. Additional experiments with smaller holes and higher pressures (138 to 345 kPa [20 to 50 psi]) are required to determine the smallest leaks that can be located over distances of several hundred feet. The current experiments indicate that improved phase-unwrapping algorithms and/or lower noise instrumentation are required to optimize system performance.

PLUNGING WATER JETS: EVALUATING AN INNOVATIVE, HIGH CURRENT, DIVERSIONARY OIL BOOM

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INTRODUCTION

Typical curtain booms begin failing to contain spilled oil in currents not much above 1.1 miles per hour, and many skimmers begin to fail in currents not much above 3.5 mph. However, many water bodies, including streams, large rivers, and estuaries, have currents well in excess of 1.1 mph. The U.S. Environmental Protection Agency's Risk Reduction Engineering Laboratory had previously tested an innovative diversionary system based on vertical, plunging water jets and found it capable of moving floating, spilled oil across small streams into areas of low current (such as the inside of river bends) where conventional cleanup technology works well. The results of scaling the system up by a factor of ten (e.g., from a 0.75" up to a 6.0" jet nozzle inside diameter) and evaluating it at three current speeds from 0.6 to 4.2 miles per hour in the Detroit-St. Clair River system are summarized here. Even in the presence of these larger turbulence scales and intensities, single plunging water jets were found to be capable of diverting floating pollutants over thirty feet in the presence of medium river currents. Multiple jets arranged en echelon were demonstrably capable of diverting material much farther.

A plunging water jet is created by directing a stream of high velocity water (about 35 feet per second) downwards through a nozzle mounted three feet above the surface of floating spilled oil. The vertical jet of water entrains air and carries it below the water surface to some equilibrium depth. The formerly entrained, air bubbles floating back toward the surface create a rising, vertical water current that becomes horizontal at the water surface. This resultant horizontal surface current moves floating matter such as spilled oil radially out from the jet's point of impact (thus clearing a circular area centered on the jet's point of impact). When the jet moves relative to the (undisturbed) water surface, the cleared circular area is deformed into a parabola with the horizontal surface current flowing perpendicularly out on both sides from the axis of the "wake" (the track of the jet across the river surface). The surface current resulting from one or more water jets can be used to clear spilled oil and other floating contaminants from a given area (such as a water intake or a diver entry point). Conversely, it can be used to thicken floating contaminants in order to make various removal devices more effective and to increase the effective sweep width of moving oil skimmers. In particular, since it is little affected by non-breaking waves and floating debris, a jet can be used to divert spilled oil in streams of all sizes and in river currents well in excess of what a conventional boom can tolerate.

The plunging water jet concept was first envisaged in 1978 by Michael G. Johnson (Johnson's patent is now held by Douglas Engineering of 181-C Mayhew Way, Walnut Creek, CA 94596). The U.S. Environmental Protection Agency then began to sponsor a series of initial feasibility tests which

culminated in 1983 in a 3/4 inch nozzle system demonstrated in small local streams and a local estuary. Based on this work, the EPA published in 1984 a field manual for the fabrication and use of a 3/4 inch diameter nozzle through which water flowed at about 80 gallons per minute (Ref. 1). This combination yielded a diversion distance of about twelve feet in currents of two miles per hour. In another application, three pairs of jets were also used to increase the effective sweep width of the US Coast Guard's six mile per hour "Zero Relative Velocity" Skimmer. Concurrently, Dr. Richard Hires of Stevens Institute of Technology reported in 1980 an analysis of his excellent and extensive series of observations of 1/4, 3/8 and 1/2 inch diameter nozzles at the Davidson Laboratory's tow tank facility (2).

METHODOLOGY

The objective of the 1992 field work described here was to evaluate the effectiveness of plunging water jets with much larger diameter nozzles and higher flow rates when used on simulated spills into a large, higher current river system (the Detroit-St. Clair Rivers) where natural turbulence scales are greater than in areas than hitherto examined. The nozzle diameters were increased from the former maximum of 3/4 of an inch to six inches and the flow rates through the nozzles from 80 to 1714 gallons per minute. Three river current speeds from 0.6 to 4.2 miles per hour were observed during this study.

The primary equipment consisted of a six-inch diameter, CCN150 submersible pump (rated at 2,250 gallons per minute under an eighty-foot head and driven by a portable, diesel-powered hydraulic system) that fed river water through a six-inch diameter flexible hose (and a turbine flow meter with a pressure gauge) to a manifold supplying four vertical, poly-vinyl chloride nozzles (of 2", 3", 4", and 6" inside diameter) controlled by individual ball valves. The manifold was strapped to the underside of a guyed, four-inch, steel, box beam suspended horizontally, at right angles outboard, from the side of a thirty-six foot long work vessel. Flow rate through whichever nozzle's ball valve was open could be varied by changing the throttle settings of the pump's hydraulic power pack. Small pine chips (intended for pet bedding) and a powdered sorbent (made from cellulose fiber and expanded perlite, and treated to be oleophilic and hydrophobic) were both used as floating tracers to outline the limits of the jet's parabolic area of influence. Floating polypropylene lines supported at five-foot intervals by fluorescent painted gallon jugs were used to provide both longitudinal and horizontal length scales. Times and distances estimated visually both by an observer in a small boat and from photographic and video records were used to calculate speeds. Flow rates and pressures were measured directly. Grouped averages of some of the sixty-eight sets of field observations made are presented in the table. The table shows that the effect of river speed on a single jet's diversion distance increases markedly as speed exceeds two miles per hour. Jet velocity (that is, the flow of water through the nozzle) is also a very significant factor, with diversion distance increasing as jet velocity increases.

FIELD DATA SUMMARY (grouped averages)				
Nozzle Diameter (inches)	Jet Flow Rate (gpm)	Jet Velocity (fps)	River Speed (mph)	Distance Diverted (ft)
4	1400	36.4	0.7	38
4	1400	36.1	1.6	35
4	1400	36.4	4.2	13

CONCLUSIONS

This evaluation shows that plunging water jets are very effective for diverting floating spilled oil and other pollutants in large rivers.

A single, four-inch inside-diameter nozzle at flows above 1400 gallons per minute (gpm) can divert floating materials about thirty-five feet in river currents of at least one and six tenths miles per hour. This substantial improvement is three times greater than the previously demonstrated diversion distance of about twelve feet by a three-quarter inch nozzle at 80 gpm in a similar current.

In a river current of four and a quarter miles per hour (under otherwise similar conditions), the diversion distance was found to be thirteen feet. This smaller distance is also useful, especially when considered in the light of the fact that a conventional boom would fail to divert any oil under similar conditions. Because plunging water jets can be arranged to operate in echelon, multiple jets can increase the diversion distance almost any amount. At this time, plunging water jets provide the only known means of diverting floating, spilled oil in four mile per hour currents.

REFERENCES

1. Nash, J.H. and J.S. Farlow. Field Manual for Plunging Water Jet Use in Oil Spill Cleanup. EPA-600/2-84-045. U.S. Environmental Protection Agency, Cincinnati, Ohio, 1984. 20 pp.

2. Hires, R.I. An Experimental Study of Currents Generated in the Receiving Waters by Plunging Water Jets (Research report prepared for the New Jersey Department of Environmental Protection, P.O. No. P-48063; SIT-DL-80-9-2136; DL Project 4759/858). Stevens Institute of Technology, Hoboken, New Jersey, 1980. 42 pp.

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APPLICATION OF THE ELECTRON BEAM TREATMENT PROCESS TO MULTI-SOURCE HAZARDOUS WASTE LEACHATE TREATMENT

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An area of considerable interest today is the on-site treatment of multi-source hazardous waste leachates. One innovative treatment process being developed for the destruction of hazardous organic chemicals on site is high energy electron beam irradiation.

We have previously reported that the process has been shown to be very effective in destroying single solute contamination from aqueous waste streams. This paper describes a natural progression of that work to results obtained from the treatment of multi-solute leachates. The three studies to be presented describe the results obtained from: 1) an aqueous solution leachate, 2) an aqueous solution containing a 1% (by volume) dense non-aqueous phase liquid (DNAPL), and 3) an aqueous leachate with a light non-aqueous phase liquid (LNAPL) layer. For all three leachates it was possible to treat to the F039 multi-source hazardous waste leachate standards for wastewater.

The process has several advantages when compared to other treatment processes. These advantages are that complex mixtures can be treated simultaneously, and the process is not adversely affected by dissolved solids such as iron and manganese. No air emissions are produced and the process goes to completion at ambient temperatures. No organic sludge is produced and the only by-products are low molecular weight acids and possibly ketones. The process stream can be reinjected, discharged to the environment or treated in a biological wastewater treatment system (POTW).

One of the most significant features of this process is that the presence of solids does not affect the removal efficiency of the organic compounds. Therefore no pretreatment is required when suspended solids are present in the leachate or other influent streams.

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PHOTOLYSIS/BIODEGRADATION OF PCB CONTAMINATED SOILS

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Bench-scale tests were conducted to investigate the feasibility of a two-phase detoxification process that has application to the treatment of soils contaminated with polychlorinated biphenyls (PCBs). The first step in the process was to degrade the contaminants by using ultraviolet (UV) radiation facilitated by the addition of a surfactant to mobilize the contaminants. Biological degradation, the second step, was then used to further destroy organic contaminants and detoxify the soil.

UV photolysis tests were conducted independently using a medium pressure mercury (Hg) lamp, a 10 hertz (Hz) pulsed lamp and sunlight on soils with surfactant applications of 2 to 5 percent. Results from UV testing on a surface soil contaminated with about 10,000 parts per million (ppm) PCBs (Aroclor 1248) and a pit soil containing about 200 ppm PCBs varied, but in most cases showed minimal reduction of PCB concentration. The PCB reductions ranged from less than 15 percent to a maximum of 52 percent. Tests using sunlight as a UV source showed no detectable loss of PCBs after 25 days of exposure.

Biological treatment on surfactant/UV-treated and untreated soil was evaluated in two bioslurry treatment experiments. The bioslurry experiments evaluated PCB degradation on surfactant/UV-treated and untreated soils using cultures with and without inducer addition. Bioslurry treatment did not provide significantly different results for the UV-treated surface soil versus the untreated soil. Percent reductions of PCBs were highest for an untreated soil containing 350 ppm PCBs which gave 70, 20 and 30 percent reduction of the di-, tri- and tetra-PCBs, respectively. In the enhanced bioslurry experiment, the addition of 1,000 ppm biphenyl stimulated greater reduction in PCB concentrations on the same soil.

The results of bench-scale testing on degradation of PCBs using UV photolysis and biological treatment will be presented. Experimental results will be detailed and data on concentration of contaminant as a function of treatment time will be displayed along with breakdown of PCB homolog data showing comparison of treatment affects on individual PCB homologs for Aroclor 1248.

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USEPA - DOE Joint Assessment Program

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The United States Environmental Protection Agency and the Department of Energy have entered into an interagency agreement to join the EPA's Waste Minimization Assessment Centers (WMAC) Program with DOE's Energy and Diagnostic Centers Program (EADC), forming the Industrial Assessment Centers (IAC) Program, combining pollution prevention assessments and energy audits into industrial assessments. These assessments are performed by university staff and engineering students to qualifying small to medium sized manufacturers in SIC codes 20-39. During 1994, six universities have been selected to launch the pilot combined program. These are Colorado State University, University of Tennessee, University of Massachusetts at Amherst, University of Wisconsin at Milwaukee, University of Texas at College Station and Oregon State University. Each of these Centers will perform ten industrial assessments in the pilot year.

Colorado State University and the University of Tennessee have performed both pollution prevention and energy assessments through WMAC and EADC programs. These two experienced schools performed test assessments in FY93 to examine different approaches to conducting these industrial evaluations. One of these test assessments is presented in this poster.

This assessment was performed by Colorado State University at a plant that manufactures telescopic sights and mounting hardware. From this assessment, one major pollution prevention opportunity is phase separation of the spent cutting fluid by acid treatment. A major energy conservation opportunity is reducing compressed air leaks.

For further information, please contact the EPA project officer, Emma Lou George, Phone (513) 569-7578 or Fax (513) 569-7111.

DECISION-SUPPORT SOFTWARE FOR SOIL VAPOR EXTRACTION TECHNOLOGY APPLICATION: HYPERVENTILATE

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ABSTRACT

Soil vapor extraction (SVE) is an in situ corrective action technology that can remove volatile organic compounds (VOC) and selected residual petroleum hydrocarbons from unsaturated soils. The EPA Office of Underground Storage Tanks and Shell Oil Company entered into a Cooperative Research and Development Agreement under the Federal Technology Transfer Act to develop a decision-support computer software which has been termed "HyperVentilate". The computer program was designed to assist regulators and underground storage tanks (UST) owners in evaluating whether SVE is an appropriate cleanup technology for use at leaking UST sites. It is an interactive, software guidance system for evaluating the feasibility of using SVE at a specific site based on site and contaminant characteristics.

The objective of HyperVentilate is to guide the user through a systematic, iterative evaluation to determine the feasibility of using SVE at a given site. The software utilizes data provided by the user to develop a rough approximation of the system's desired and maximum removal rates. It can provide two estimates of the minimum number of vapor extraction wells needed to achieve remediation. The first estimate is developed by simply comparing the anticipated extraction well radius of influence with the radial area of contamination. The second estimate is based on a calculation of the volume of air that needs to be extracted from the soil to remove residual contamination. The user is ultimately responsible for deciding if the estimates generated by the software are technically and economically practical for a particular site. HyperVentilate is primarily a software tool for evaluating SVE as a remediation alternative; it is not intended to be a detailed SVE modeling or design tool.

A report entitled, "Decision-Support Software for Soil Vapor Extraction Technology Application: HyperVentilate," (EPA/600/R-93/028) provides guidance in evaluating the use of the IBM-compatible version of HyperVentilate. In addition, an overview of SVE principles and procedures is presented along with the basic model principles and a sensitivity analysis of the software. A sample application is also presented by using data from an actual UST site. The case study demonstrates how to estimate and determine input parameters, goes through the steps involved in deriving estimates to evaluate whether SVE is appropriate, and discusses interpretation of the case study results.

REMOVAL OF ORGANIC COMPOUNDS FROM DRINKING WATER USING MEMBRANE TECHNOLOGY

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Today there is a great deal of public concern regarding drinking water. The public is not only concerned with taste-and-odor causing compounds but is also concerned with many cancer-causing compounds that increasingly find their way into the nation's drinking water. The Systems and Field Evaluation Branch of the Drinking Water Research Division (DWRD) is responsible for evaluating various technologies that may be feasible for meeting Maximum Contaminant Levels. Several membrane processes are under investigation to determine their effectiveness in removing synthetic organic contaminants as well as inorganics from drinking water.

Reverse osmosis is the reverse of the natural process of osmosis. Reverse osmosis can be described as the flow of water (or some other solvent) across a boundary from a more concentrated side to the less concentrated side, as the result of the application of pressure to the more concentrated side. Reverse osmosis membranes have shown promise in two DWRD studies. In a laboratory setting, these membranes were used to treat multisolute, aqueous solutions of alkanes, alkenes, aromatics and pesticides. At a field-scale research site in Suffolk County, New York, removal of agricultural contaminants was accomplished through the use of membranes. Both laboratory and field scale studies indicated that reverse osmosis shows promise for removal of organic and inorganic contaminants from drinking water.

Pervaporation is yet another membrane process whereby a liquid mixture is in direct contact with a membrane. On the other side of the membrane is a vacuum which pulls the permeate out of the liquid mixture. In this case the organic contaminants might be contained in a very small, highly concentrated volume. There is interest in this technology for drinking water purposes because of it's potential for side-stream-reduction. Therefore future studies will address pervaporation from both an organic' s removal perspective as well as a pollution prevention perspective.

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PACKAGED WATER TREATMENT PLANT OPERATION AND FIELD DATA DOCUMENTATION PROJECT

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The "Packaged Water Treatment Plant Operation and Field Data Documentation Project" (the project) was a cooperative effort between the American Water Works Association (AWWA) and the United States Environmental Protection Agency (EPA), Drinking Water Research Division (DWRD).

In order to study the problems facing small communities, both today and in the near future, as they try to comply with new water regulations, this project was designed to examine existing, in place water treatment systems to determine their capability in meeting current and future regulations. The primary goal was to gather reliable and verifiable data regarding the long-term cost and performance of package water treatment plants being operated by small systems.

The project evaluated 48 small system package plants. The project used the EPA definition of a small water system as under 1000 connections or fewer than 3,300 people served. To allow for the identification of possible differences in treatment approaches caused by differences in water quality, funding availability and economic support, between the smallest and the largest of these small water systems, they were divided into three population ranges 25-500, 501-1,000, and 1,001 - 3,300.

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RISK REDUCTION LABORATORY (RREL), DRINKING WATER TECHNOLOGY ACTIVITIES - U.S. EPA

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This poster conveys the activity of the Drinking Water Research Division (DWRD). DWRD, of Risk Reduction Engineering Laboratory (RREL) plans, coordinates and conducts a national program to provide the technology necessary to help prepare the primary and secondary regulations for drinking water. The Division has the responsibility for a program that integrates chemistry, engineering, microbiology, and cost-effective techniques for assuring the delivery of safe drinking water to reduce the risk of chemically and microbiologically induced health effects to the public.

The Division conducts both intramural and extramural research to establish practices for the control and removal of contaminants, and for the prevention of water quality deterioration during storage and distribution in the most economical manner. The Division operates its own inhouse pilot facilities, chemistry, and microbiology laboratories, as part of the intramural program.

Major areas of research include disinfectants, disinfection by-products, corrosion control, small system technologies, distribution systems, bacteria, viruses and protozoa.

The Division works closely with municipal and county activities that treat raw water and operate water supply facilities, as well as with universities, professional, and private organizations that conduct control technology activities. The Division maintains technical liaison with the Office of Ground Water and Drinking Water (OGWDW) in the Office of Water (OW) to ensure timely completion of the regulatory and compliance requirements of the Safe Drinking Water Act (SDWA).

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Pollution Prevention Research Branch Program

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KEY ISSUE: ***How should consumer and industrial products and services be designed, manufactured, and used for a minimal effect on the environment?***

Since 1988, the Pollution Prevention Research Branch (PPRB) at USEPA's Risk Reduction Engineering Laboratory in Cincinnati, Ohio, has supported projects and provided technical assistance to encourage the development and adoption of technologies, products, and pollution prevention (P2) techniques to reduce environmental pollution. To date, approximately $10 million dollars have been expended to support this program. The program focuses on five major areas which include:

Cleaner Production Technologies: To develop, demonstrate and evaluate innovative processes for reducing pollution through source reduction.

Cleaner Products: To support the design and development of products whose manufacture, use, recycle and disposal represent reduced impacts on the environment.

Tools to Support Pollution Prevention: To develop life cycle assessment and measurement methodologies to guide pollution prevention strategies.

Pollution Prevention Assessments: To identify P2 opportunities in a variety of industries and to transfer that technical information to assist others in implementing pollution prevention.

Cooperative P2 Projects with Other Federal Agencies: To promote pollution prevention in other Federal Agencies through cooperative research, training, and demonstration projects.

This poster displays personnel and major areas of research through pictures and narrative. Handouts will be available describing the ongoing projects and Branch publications. Members of the Branch will be available periodically for discussion.

For further information, please contact Emma Lou George, Phone (513) 569-7578, Fax (513) 569-7111 or Harry Freeman, Phone (513) 569-7215.

ABSTRACT

USING DATA QUALITY OBJECTIVES (DQOs) TO SEARCH FOR HOT SPOTS

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Each year the U. S. Environmental Protection Agency and the regulated community spend approximately $5 billion collecting environmental data for scientific research, regulatory decision making, and regulatory compliance and most importantly in Superfund cleanup and remediation of hazardous sites. The goal of EPA and the regulated community is to minimize expenditures related to data collection by eliminating unnecessary, duplicative or overly precise data and at the same time collect data of sufficient quality to support defensible decision making. These goals can be accomplished by ascertaining the type, quality and quantity of data necessary to address the problem before the study begins.

The focus of this Poster presentation is to demonstrate the development and implementation of a quality system through the DQO process developed specifically for Superfund. The Data Quality Objective (DQO) Process for Superfund was developed by the Quality Assurance Management Staff for the Office of Solid Waste and Emergency Response's Hazardous Site Control Division, with input from the DQO Workgroup comprised of the 10 Regions and Headquarters' Environmental Services and Waste Management Divisions.

The DQO process is a scientific and legally defensible data collection planning process to help users decide what type, quality, and quantity of data will be sufficient for environmental decision making. The DQO process provides a logical framework for planning multiple field investigations, thereby improving cross-program response planning and allowing optimal cross program data useability, which are important goals of the Superfund Accelerated Cleanup Model (SACM).

The poster will apply the DQO process to the Leadbury Superfund Site. The DQO process will demonstrate its usefulness as a tool and an effective means by which managers and technical staff may plan and design a more efficient and timely sampling and analysis program that is consistent with the integrated site assessment and accelerated response activities of the Superfund Accelerated Cleanup Model (SACM).

The poster will look at the problem of searching for a highly contaminated area (hot spot) within a much larger area of minimal contamination. The poster shows how the initial assumptions on the size and shape of the hotspot are crucial to the design of the data collection activity. Different scenarios are explored and some recommendations on optimal sampling schemes will be made.

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