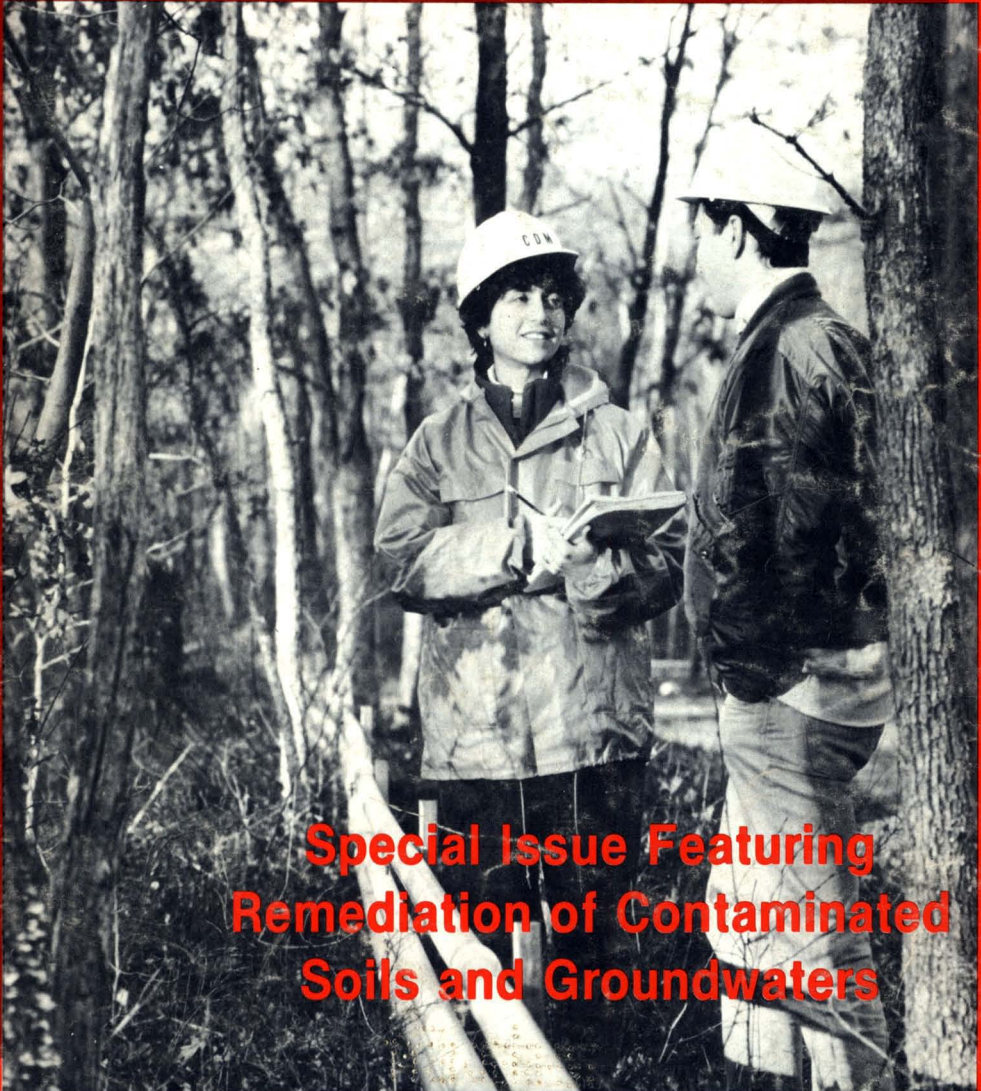


AUGUST 1992

ENVIRONMENTAL PROGRESS



**Special Issue Featuring
Remediation of Contaminated
Soils and Groundwaters**

Discussing remedial design services for groundwater and soil contamination (See page A6)
Photo by Tom Graves, courtesy of CDM Inc., Cambridge, MA

PROCESS CONTROL THEORY AND THE CPI...

**CHEMICAL PROCESS
CONTROL—CPCIV**

Edited by
Yaman Arkun
W. Harmon Ray

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Despite its advances, process control theory has been slow to realize its full potential in the chemical processing industry. Control experts have “theorized” themselves out of the industrial loop. Control remains mostly an afterthought to process design. Yet safety and economics clearly demand more high-performance, non-linear control techniques in the CPI. Those are among the important issues addressed in the new volume of Chemical Process Control—CPCIV. This 700-page compendium contains 37 of the most significant papers from the Fourth International Conference on Chemical Process Control. It covers virtually every topic in the field that chemical engineers should know about. From inventory control in Japanese plants to modeling in neurobiology, these papers sum up five years of the very latest control applications from industry, academia, and government. This fully indexed volume covers:

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Special Remediation of Contaminated Soils and Groundwaters issue

Robert W. Peters, Guest Editor

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1993

Now is the time to plan your entry, even though the judging is a few months away (February '93). Any person, firm, institution or government agency can enter, whether or not

affiliated with the Academy, **any** type of environmental engineering project — air, water supply, wastewater, hazardous waste, industrial hygiene, radiation protection or solid waste management.

The hallmark of the Academy's Award and the principal judging criteria include:

- Demonstration of an **integrated approach** that considers all environmental media — air, water and land.
- **Quality** as evidenced by the degree of user satisfaction and proven performance.
- Contribution to **social and economic advancement**.
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Six GRAND PRIZES will be presented for excellence in — **Research, Planning, Design, Operations/Management, Small Projects and University Research**. Plus, other entries may qualify for HONOR AWARDS.

The Academy will actively promote the winning entries by featuring them in its exhibit at trade shows and conventions. Winning entries will also be featured in national publications. The public relations value is considerable.

Obtain your entry form and details by writing to Academy headquarters: 130 Holiday Court, Suite 100, Annapolis, MD or call 410-266-3311.

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*Excellence in
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This special issue of *Environmental Progress* is devoted solely to cleanup on contaminated soils and groundwaters. Conventional excavation and incineration with subsequent disposal in a licensed landfill is time-consuming, energy intensive and very expensive. New cost-effective technologies are needed for remediation of the many identified contaminated sites across our nation. Innovative treatment technologies are addressed in this special issue. The paradigm of employing synthetic feed-streams of high purity to simulate waste feed streams is highlighted in this issue's editorial. The papers contained in this special issue were presented at the AIChE Summer National Meeting (Pittsburgh) and the AIChE Annual Meeting (Los Angeles) in 1991. Of the thirty-four manuscripts submitted, thirteen were accepted for publication in this issue. All thirty-four papers were peer reviewed.

The first paper appearing in this issue addresses the Superfund remedy selection process. This paper is followed by an evaluation of PCB remediation technologies. In the remaining papers, many innovative remediation technologies and applications are covered, including granular activated carbon treatment for explosives, use of hydraulically installed lysimeters to obtain representative soil water samples, ultrasonic treatment for detoxifying groundwaters, effect of chemical pretreatment on anaerobic biodegradation of refractory organic compounds, supercritical extraction of polynuclear aromatic hydrocarbons, the B.E.S.T.[™] solvent extraction process, adsorption/desorption of metals from soil, electrokinetic removal of heavy metals, and soil vacuum extraction. These papers provide state-of-the-art technology for remediation of contaminated soils and groundwaters. They also indicate the broad scope of the remediation field, with the papers authored by professional staff in academia, research institutions/national laboratories, consulting firms, industry, and government agencies.

I wish to personally thank the authors for their cooperation in the preparation of their manuscripts for this special issue. I am especially grateful to the peer reviewers who assisted in the selection of the papers accepted for publication and helped to improve the technical quality of the papers. The entire issue is dedicated to all people interested in the field of soil and groundwater remediation.

Robert W. Peters,
Guest Editor

Toward a Waste Treatment Research Paradigm in Academia

Louis J. Thibodeaux

At a recent conference, a speaker was proposing continuing research on an exotic catalyst for the thermal destruction of chlorinated hydrocarbons. In the proof-of-concept stage, several nines percent destruction efficiency was achieved. However, in response to a question, he admitted the process was constrained to a pure feed stream.

Investigators at numerous academic institutions are now performing waste treatment research using basically the same paradigm for chemical product/process development where extensive chemical separations to prepare the feed and purify the product are necessary. A dozen nines in efficiency will not render the catalytic process an economic reality since conventional incineration, in a rotary kiln, requires little feed preparation. The research should be discontinued immediately. Chemical product development projects typically progress through six somewhat distinct phases. These phases for waste treatment development are: (1) idea, (2) proof-of-concept, (3) bench-scale testing, (4) pilot-scale testing, (5) field demonstration, and (6) commercialization.

The research director and the investigators need to forge a relationship that fosters intellectual honesty since their goals are often times at odds. The former is interested in developing cost-effective, new technologies for waste treatment, while the latter is primarily interested in receiving funds to produce manuscripts and students.

The mutual understanding of a few simple facts and guidelines produces a clear paradigm for waste treatment research:

- the product is nearly always valueless;
- the feed is almost always "dirty";
- use actual waste as feed, never spiked sand as a surrogate soil for example;
- get expert advice on materials handling problems early; and
- multiple processing steps is usually a fatal flaw in the process design.

This is a partial list. The last item is one in several possible fatal flaws, so that an independent party should perform a rudimentary robustness check of a realistic operating scenario,

including a cost comparison with the current available technologies. In a more extensive evaluation, systems analysis is performed to identify fatal flaws and limitations in the processing scheme, as well as performing cost analyses. In general, the project should be critically evaluated after each stage prior to proceeding further.

We must also question the wisdom of using the conventional six-step idea-to-commercialization approach. For example, consider the case of *in situ* bioremediation of contaminated bed sediment in a marine setting. Organisms are available that have shown promise of destroying the primary toxic contaminants and the PIs are seeking funds for the proof-of-concept phase. Isn't it reasonable at this juncture to have the PIs assume that the microorganisms can do a six-nines conversion of the toxic contaminants and proceed immediately to Step 5, which is field demonstration, so as to concentrate on the engineering technology and associated costs of implementing a "facility" on the offshore site in order to: seed the bed with microorganisms and maintain the culture, provide and control the nutrient levels, monitor the conversion progress, etc., without substantial disturbance of the bed so as to release toxic materials to the water column. As this example illustrates, leapfrogging to step 5, as part of the research paradigm reality check, may shelve the project or cause its redirection. Proceeding algorithm-like through Steps 2, 3, and 4 developing an elegantly tailored microorganism system to later realize with back-of-the-envelope engineering analysis at the eleventh hour that an obvious fatal flaw to implementation existed, suggested a gross lack of director involvement in the research program.

Limited resources force the research director to make early, hard decisions eliminating ideas with little pay-off potential. A clear research paradigm aids correct decisions and those investigators unwilling to operate under this altered and much constrained research paradigm should look elsewhere for funding.

Louis J. Thibodeaux, Ph.D., is Jesse Coates Professor of Chemical Engineering and Director, Hazardous Substance Research Center, South/Southwest, at Louisiana State University, Baton Rouge, LA 70803.

Remedial Design Services for Groundwater and Soil Contamination

Camp, Dresser & McKee Inc., (CDM) of Cambridge, Massachusetts, has developed advanced technical capabilities in all phases of remedial design for contaminated soils, groundwater, surface water, sediment, and airborne pollutants.

CDM engineers, scientists, and planners have worked with the in-house environmental staff of numerous industrial clients to expedite remedial designs.

Groundwater remediation

CDM has designed air and steam stripping and activated carbon adsorption treatment processes for alleviating groundwater contamination problems nationwide. For especially complex treatment problems they have explored even more sophisticated treatment technologies. They are currently using an ozone-hydrogen peroxide advanced

oxidation process, combined with biological treatment, to clean up an aquifer contaminated by one of the largest gasoline spills in New York State.

To enhance their aquifer remediation programs, they have developed highly advanced computer groundwater models that illustrate how aquifer systems really work: in three dimensions. Their DYNFLOW model predicts groundwater flow vertically and horizontally; the DYNTRAK model maps the movement of contaminants through the aquifer. These models are able to delineate contaminant plumes from multiple sources.

Soil Contamination

CDM has also designed a wide range of soil remediation solutions using technologies as diverse as the contaminant problems themselves. For one industrial client, they designed an innovative - and cost-effective - vacuum

extraction system to air-strip volatile organic contaminations from soils *in situ* without excavation, allowing plant operations to continue undisturbed. At an electric utilities site with high levels of pentachlorophenol in the soil, CDM specialists successfully pilot-tested a unique low-temperature thermal treatment system and developed a plan for solidification and capping of on-site waste material.

At a number of industrial sites, they are using innovative bioremediation processes for effective on-site soil treatment.

Air Emissions

CDM also provides full-service air quality management and emissions control, including ambient air monitoring and dispersion modeling in support of permitting for hazardous waste incinerators.

New Degrees in Environmental Technology Offered at NYIT

Two new degrees in environmental technology are offered by New York Institute of Technology's School of Engineering and Technology, beginning this fall.

Heading the new environmental technology programs is Prof. Stanley M. Greenwald, P.E., who stated that "the rush by government agencies and industry to clean up the polluted and contaminated environment will not necessarily insure competitiveness in world markets nor a permanently clean environment".

The Bachelor of Technology degree is a traditional engineering technology program suitable for high school or community college graduates and military service personnel with interest in practical solutions to environmental problems. The Master of Science degree will provide advanced training in pollution control, alternative fuels, waste management or regulatory compliance for practicing professionals or individuals looking to change career directions.

Further information can be obtained by calling the Office of Admissions at 1-800-345-NYIT or the Dean's office (516) 686-7931.

Wastewater Treatment System Remains In Compliance During Cold Weather Operation

Cold temperatures can turn an otherwise well operating wastewater facility into a lower performance facility that often is not in compliance during the winter months. Sybron Chemicals Inc., Birmingham, N.J., has introduced a BI-CHEM® 1738 CW a custom blend of selectively adapted bacterial cultures that has been developed to enhance removal efficiencies during lower temperatures.

The effective, psychophilic (cold-loving) blend of bacterial cultures works year-round to eliminate cold temperature non-compliance problems occurring during the winter months. Sybron BI-CHEM bacterial cultures have been selectively adapted to enhance the cold weather removal of emulsifiers, phenols, and detergents typically found in the wastewaters of chemical, petrochemical, refining, pulp and paper, food processing and textile industries.

With the onset of cold temperatures, most chemical and biochemical reactions exhibit a predictable slowdown. Sybron has found that BI-

CHEM 1738, introduced at regular intervals prior the onset of cold weather, permits the culture to acclimate to improve the rate of waste reduction. During cold periods, BI-CHEM 1738 adapts quickly to thermal shocks that may reduce the ambient temperature extremes from 80° F to 39° F (27° C to 3.9°C).

Severe temperature drops slow the transport of nutrients and oxygen across the cell membrane of the bacteria and reduce the effectiveness of the culture. Membranes which typically contain high concentrations of saturated fatty acids interfere with nutrient transfer by becoming more rigid at lower temperatures. BI-CHEM 1738, which contains a much higher concentration of unsaturated fatty acids in the cell membrane, reduces the impact of low temperatures on nutrient transport by permitting the cell membrane to remain more fluid.

For more information contact Mark Krupka, Sybron Chemicals Inc., Birmingham Road, Birmingham, N.J. 08011. Phone (toll-free) 1-800-678-0020 or call (609) 893-1100.

Hazardous Waste Management, Charles A. Wentz, McGraw-Hill, New York, N.Y., 461 pages. ISBN 0-07-069291-2, U.S. List Price: \$46.95 (1989).

Up to this point, I have been unable to find a book that I felt comfortable using as a text for a hazardous waste course for no book (in my opinion) had been written for that purpose. Consequently, I was delighted to read in the preface of the text:

... The primary purpose of Hazardous Waste Management is to integrate a broad field into a single book that deals with all phases of this important subject...

This textbook (emphasis added by the reviewer) has been written at a level suitable for the senior undergraduate or beginning graduate student who has knowledge of the basic fundamentals of science and engineering.

The material (in the text) brings together legislation, regulations, technology and business matters relating to hazardous wastes management. In order to understand this dynamic field better, numerous case studies have been provided, which should assist the reader in relating to actual environmental situations.

The author has achieved his stated purpose, writing 14 different chapters covering all the significant aspects of hazardous waste disposal. He provides enough information to educate the reader, but he does not suffocate him with the voluminous amount of detail that is available. This reviewer is well aware of the amount that could have been written, as more than one book devoted solely on the topic of each chapter rests on his bookshelf.

One desirable aspect of the book is the inclusion of problems/exercises at the end of each chapter and provision of a *Solutions Manual* for the instructor. Clearly, these exercises enhance the book's value as a text.

The first chapter starts rather slowly with the RCRA definition of hazardous waste. Although this may be an appropriate starting point (i.e., defining the legal aspects of the problem), I would personally have "overviewed" the topic before diving into details (especially details as boring as the law), even though they are very important. Additionally, I question Wentz's inclusion of almost five pages of text on the reactor accident at Seveso, Italy, where dioxin contamination resulted. I will admit that one result of the accident was

the creation of hazardous waste to be disposed of, but that was really a tangential problem to the health risk caused by the dioxins. The second chapter, devoted to Risk Assessment, is a concise discussion of the topic, but unfortunately it is too concise, thus manifesting the problem noted in the opening paragraph. I said that Wentz avoided overwhelming the reader with information, but there is a fine line between too little and too much information. However, I wished for a little more information here perhaps in the form of a numerical example of risk calculation, especially of risk that might occur from hazardous waste management or disposal. The two examples given in the chapter deal with virgin chemicals (ethylene dibromide and lead) resulting from use, not from waste disposal.

Chapter 3 is a short one, overviewing all of the significant Federal environmental laws from the Rivers and Harbors Act of 1899 to the 1986 Amendments to CERCLA. Approximately one page is devoted to giving the reader an overview of each law. Wentz followed with a whole chapter devoted solely to TSCA, RCRA, and CERCLA/SARA. This is very appropriate because these three laws are the keys to the text (or at least they are the legal keys). Surprisingly, Wentz also included some material which is questionable regarding its relation to hazardous waste. The material consists of a discussion of the contamination of the Life Sciences Plant at Hopewell, Virginia, in 1974. That was an interesting problem (and a most significant pollution problem for the local POTW and the chemical plant employees) but until the plant was razed, it was not a hazardous waste problem.

Chapter 5 is a strange combination of hazardous waste characterization and site assessment. The first 10 pages of the chapter are devoted to a discussion of what characteristics make a waste hazardous. I would have placed this section in the previous chapter in which the laws governing hazardous waste were discussed, and then continue with site assessment as the author did in a separate chapter. In the site assessment section, he thoroughly reviewed two interesting contaminated sites: (1) PCB contamination at a GE site in Oakland, California, and (2) solvent spills at the Biocraft Laboratories Plant in Waldeck, New Jersey.

Chapter 6 is the real beginning of the text (at least from the technical viewpoint of hazardous waste management). It is titled "Waste Management and Resource Recovery" in which

manifestation of the new concept of the positive aspects of waste disposal are preventing its generation are addressed. Interestingly, early in the chapter, Wentz discusses government policy which is a dangerous but necessary process because it changes so quickly. Government policy is even more volatile in the field of waste management. Indeed, the U.S. EPA has established a new office of "Pollution Prevention", a little more far reaching concept than simple waste minimization. Several bills on this topic are before Congress at the moment.

Successive chapters deal with Chemical, Physical, and Biological Treatment (dealing mainly with aqueous hazardous waste streams) and Thermal Processes (including incineration of PCBs under TSCA). Not included in the incineration discussion, however, was an intensive discourse on air pollutants and their control, otherwise this is an excellent chapter. Also included was a very good discussion of Chemical Waste Management's incinerator ships, Vulcanis I and Vulcanis II, transportation of hazardous waste including placarding and manifesting and emergency aspects. Another chapter dealt with groundwater contamination, detection, and sampling.

Chapters 10 and 11 are devoted to what one chemical engineer has called "perpetual" storage: Landfill Disposal and Deepwell Injection. In chapter 11, Wentz begins his discussion with a case study — The Love Canal — to show what can happen when landfills are improperly managed.

The book ends with two not very hopeful chapters. In chapter 14, Wentz discusses the very different topics of "Process Selection" and "Facility Siting" The problem here is the NIMBY Syndrome and the great public fear of hazardous chemicals/wastes. Indeed, Wentz himself painfully experienced public wrath when he tried to permit an incinerator in North Dakota.

Frankly, I note that there are four short appendices parenthetically. I routinely chastise authors for including long lists or excerpts from the Register of Material that is not essential to the reader and could easily be obtained from the source document. Such is not the case here. Wentz lists: (A) priority pollutants, (B) hazardous waste from non-specific sources, (C) hazardous waste from specific sources, and (D) listing of EPA hazardous waste from commercial chemical products, intermediates, and residues. All of the appendices contain useful data and utilize only 25 pages.

In summary, although I feel there are

topics or organizations I would change (or have written differently) I could never have produced such an excellent book. As I said at the beginning, the author has produced the first book on hazardous waste that I could cheerfully adopt as a course text. *Hazardous Waste Management* contains a good, basic discussion of the laws, technology, and background of the hazardous waste problem and its solution (or at least management). The use of case histories provide an excellent point of departure from class discussion to be followed by assignment of the problem/exercise at the end of each chapter. I personally would supplement the book with outside readings in areas I wanted to cover more thoroughly, but would be confident that the student had the basic knowledge from reading the text to allow him to handle that subject.

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Contamination of Ground Water: Prevention, Assessment, Restoration
Pollution Technology Review No. 184
Michael Barcelona, Allen Wehrmann,
Joseph F. Keely, and Wayne A. Pettyjohn, Noyes Data Corp. Park Ridge, NJ, 213 pages, ISBN 0-8155-1243-0, U.S. List Price: \$ 45.00 (1990)

Groundwater contamination has been detected in every state and the number of cases is on the increase. The subsurface environment of groundwater is characterized by a complex interplay of physical, geochemical, and biological effects that govern the release, transport, and fate of a variety of chemicals. This book addresses three main areas: (1) prevention of contamination, (2) assessment of the extent of contamination, and (3) restoration of groundwater quality. The stated purpose of the book is "to discuss measures that can be taken to ensure that uncertainties do not undermine our ability to make reliable predictions about the response of contaminants to various corrective or preventive measures". The authors are from the Illinois State Water Survey, the U.S. Environmental Protection Agency, and Oklahoma State University. They are experienced and well qualified in the subject area of this book.

The book is broken into two parts and contains nine chapters and an appendix.

Part I addresses the framework for protecting groundwater resources while

Part II addresses the scientific and technical background for assessing and protecting the quality of groundwater resources.

In Part I, Chapter 1 begins with groundwater contamination addressing definitions (such as contaminant and groundwater contamination), the extent of groundwater contamination, the general mechanism of groundwater contamination, sources of groundwater contamination, and movement of contaminants in groundwater. Chapter 2 deals with groundwater quality investigations (regional, local, or site), protocol for conducting the investigation, and descriptions and results from several investigations. Chapter 3 addresses groundwater restoration covering topics such as subsurface effects on contaminant mobility, physical containment techniques, hydrodynamic controls, withdrawal and treatment, *in situ* treatment techniques, and treatment trains.

Part II begins with Chapter 4 on basic hydrogeology in which precipitation, infiltration, surface water, groundwater, and the relationship between surface water and groundwater are discussed. Chapter 5 concerns monitoring well design and construction, covering groundwater monitoring program goals, monitoring well design components, and monitoring well drilling techniques. Groundwater sampling is discussed in Chapter 6 beginning with an introduction and subsequent discussions on the establishment of a sampling point and elements of the sampling protocol. The use of groundwater tracers is discussed in Chapter 7. Topics covered in this chapter include: general characteristics of tracers, public health considerations, direction of water movement, travel time, sorption phenomena of tracers, hydrodynamic and molecular dispersion, practical aspects, and types of tracers. Chapter 8 discusses the use of models in managing groundwater protection programs and covers the utility of models; assumption, limitation and quality control; applications in practical settings; and liabilities, costs, and recommendations for managers. Chapter 9 deals with basic geology. Topics discussed in this chapter include: geologic maps and cross-sections; groundwater in igneous rocks, metamorphic rocks, sedimentary rocks, sedimentary rocks and unconsolidated sediments; the relationship between geology, climate, and groundwater quality; minerals; rocks; weathering; erosion and deposition; geologic structure; and geologic time. The book concludes with an appendix listing sources of information about groundwa-

ter contamination. Further, each chapter provides a reference section listing all the references cited in that chapter.

The book contains a vast array and wealth of information and should be a useful reference book to both inexperienced and experienced people in the field of groundwater contamination and remediation.

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Experimental Design in Biotechnology, Statistics: Textbooks and Monographs, Volume 105 Perry D. Haaland Marcel Dekker, Inc., New York, NY, 259 pages [ISBN No.: 0-8247-7881-2] U.S. List Price: \$ 89.75 (1989).

While engineers have long relied on empirical experimentation to develop processes, scientists have often argued that a complete understanding of a process is needed before it can be properly optimized. Consequently, engineers often engage in complex and expensive empirical factorial design experiments while scientists often engage in complex and expensive mechanistic studies aimed at modeling a process by attempting to reconstruct it from its component parts: a process which may ignore higher-order interactions. For complex processes where many variables can affect the output, both approaches may be difficult to apply successfully. Fortunately, in recent years, due to the development of statistics and computer programs which make their application usable by non-specialists, there are now powerful techniques available which can greatly enhance the information and efficiency of experimentation. Unfortunately, many of the statistics texts which describe these methods are difficult for the non-statistician to understand and apply to their particular problem.

This book is a welcome exception. It gives a lucid account of the experimental issues, the appropriate experimental designs, the application of statistics, and the interpretation of the results. While focussing on specific problems encountered in biotechnology, this book is very readable for the "non-expert" and may be generally applied to any complex biological problem where limited time and resources are available. The book contains 9 chapters and an appendix con-

taining specific experimental designs and statistical tests for easy reference. The introductory chapter provides an overview of difficulties inherent in collecting information-rich data, separating signals from noise, applications to actual examples in biotechnology processes, and alternative approaches for problem solving.

Chapter 2 addresses the step-by-step approach taken for optimizing *in-vivo* monoclonal antibody production. This includes a description of the problem, initial screening experiments, an optimization experiment, and a verification experiment. This example is a full factorial design experiment in which factors are assumed to have two levels (e.g., high and low).

Chapter 3 discusses clear signal designs for reducing the size of the experiment while maintaining information about two factor interactions. The optimization of a sandwich-immunoassay is used to examine the effects of a variety of fractional factorial designs and the reasons why clear signal designs are preferable.

Statistical models and methods used for separating signals from the noise are examined in Chapter 4. In this case, the stability of the enzyme-immunoassay is

examined. A variety of statistical methods are used including graphical plots and regression analyses. These methods are standard for several popular statistical packages.

Chapter 5 covers the types of experimental designs, their power and sample size, and types of potential errors. In this chapter, optimization of a cell culture system for producing monoclonal antibodies is investigated.

Chapter 6 discusses the statistical transformations which may be needed when developing an appropriate multiple regression model. This chapter is useful since this aspect of multiple regression is often mystifying to non-statisticians.

Chapter 7 addresses mixed-level designs in which one or more factors have three rather than two levels. In this case, non-orthogonal designs are considered and applied to examining factors which can affect a bioactive coating of a polyurethane surface.

Chapter 8 examines the use of iterative strategies for solving empirical problems. This chapter presents a strategy approach to determine which variables are significant by identifying important experimental factors, eliminating unimportant experimental factors, and identi-

fying near optimal settings through a series of small experiments.

The final chapter ties together the iterative strategies discussed in Chapter 8 with the experimental designs described in previous chapters. In this case, methods are combined in order to improve the stability of a microbead-based immunoassay. Finally, the Appendix lists the experimental designs used including quick reference tables for screening experiments and tests for curvature.

This book is both comprehensive, well written, and appropriate for non-experts in experimental design, statistical methods, and biotechnology. It is recommended reading for any biological scientist or engineer who wishes to begin utilizing powerful state-of-the-art statistical design methods in their experimental program in order to reduce the number of experiments needed, maximize the amount of information obtained, and properly interpret the results.

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Sources of Environmental Software

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INTRODUCTION

Software dealing with environmental pollution problems are used by environmental professionals every day. The applications include regulatory compliance, design of pollution control equipment, processing and analysis of monitoring and emission data, preparation of environmental impact assessment and emergency planning. One of the questions asked by environmental managers is: Where do I look for current pollution software dealing with pollution problems? The purpose of this paper is to discuss various sources of environmental software. Discussion also includes some examples of available software.

SOURCES OF SOFTWARE

Information of environmental software can be found in journals, trade publications, books and environmental bulletin boards. Various sources may be grouped as follows:

- (a) **Journal Reviews:** These are important sources for obtaining views on current software. Over the last ten years environmental journals have been adding a software review column or publishing a directory of available software for their readers. Software are reviewed on a regular basis in the *Journal of the Air and Waste Management Association*, *Environmental Progress*, *Pollution Engineering*, *American Industrial Hygiene Association Journal* and others. By looking at these journals one can obtain different view points on the same software. This will help in the selection of software for your particular application.

Table 1 and Table 2 are examples of software articles published in the *Journal of the Air and Waste Management Association* during 1990-91 and *Environmental Progress* during 1989-92, respectively.

- (b) **Directory:** An annual directory of environmental software is published by the *Pollution Engineering Journal* [1], the *Chemical Engineering Progress (AIChE)* [2], and *Donley Technology* [3]. These directories are detailed and include information on the application of software.

The level of details of environmental software has increased dramatically since *Pollution Engineering* began to

review programs in 1985. Early environmental programs examined in *Pollution Engineering* were merely general software packages repackaged under an environmental label. The 1992 annual review of *Pollution Engineering* gives the details of the company and its software packages related to areas of air, physical/chemical data, cost, energy analysis, fluids (air and water), comprehensive environmental data management and water. This review also gives the various aspects in which a particular software can be used.

Chemical Engineering progress software directory [2] is an important source of information for environmental software. More than 1,200 programs from vendors and chemical engineering faculties in the United States of America (U.S.), Canada, the U.K., Europe and elsewhere are covered in 1991-92 directory. The programs are divided into 27 categories. Each of these categories provide a brief description for every program. The tables in the directory also indicate how many years the program has been on the market. The information on hardware requirements, operating systems, peripheral devices, and other features such as source code availability, hot line assistance and tutorials is also included in the directory.

Donley Technology's Environmental Software Directory gives information on commercial and government software, on-line systems, and databases in the environmental field. The description, hardware and software requirements, a point of contact, and cost information for about 500 systems are listed in the annual directory (1990-91 edition). The new edition contains over 100 new systems and the updates for previously listed systems.

- (c) **Environmental Software Journal:** This quarterly journal publishes reviewed papers on environmental software. The papers include technical details, application and availability of software. The journal is published by Elsevier Science Publishers Ltd.

Table 1 Software Reviews published in Journal of the Air and Waste Management Association (AWMA) during the period 1990 and 1991

<u>NAME</u>	<u>VENDOR</u>	<u>REQUIREMENTS</u>	<u>PURPOSE/TYPES</u>
Graph Plus Ver. 1.3 etc.	Micrographix, Inc. Richardson, TX	IBM-PC, 640 Kb hard disk	presentation, graphics
Registrar, Ver. 2.0	Silton-Bookman Cupertino, CA	IBM PC with hard disk, also available in LAN format	student training, tracking system
Spectra Calc.	Galactic Indust. Corp. Salem, NH	IBM-PC with at least 512 k memory	Scientific data processing/package
Reg. Scan RCRA	Regulation Scanning Corp.	IBM-PC, MS-DOS 3.0, 400 kb of RAM, 3 MB on hard disk	It provides, in computer accessible form, the complete text of the solid waste regulations in the Code of Federal Regulations for title 40 CFR parts 240-299.
Waste Reduction Advisory System (WRAS), Ver. 2.3	Illinois Hazardous Waste Research and Information Center Savoy, Illinois	IBM-PC, 640 kb RAM, DOS 2-1 or higher, printer	It is intended for use as an interactive waste management tool designed to increase a generator's knowledge range of options for reducing and recycling industrial waste and to access citations and abstracts of articles on waste reduction.
Fluid Mechanics Programs for IBM PC, 1987 ver.	Mc-Graw Hill Book Company New York, NY	IBM-PC, MS-DOS 2.0, 64 kb of RAM	Educational programs written in BASICA.
Equil	Micromath Scientific Software Salt Lake City, Utah	IBM-PC with at least 640 k of memory	To assist the solution of complex equilibrium problems.
Airstrip, Ver. 1.2	AirStrip, Ames, IA	IBM-PC with hard disk and printer	It is represented as a design tool or air-stripping towers to be used for removal of volatile organic contaminants (VOC's) from water supplies.
MINSQ	Micromath Scientific Software Salt Lake City, Utah	IBM-PC with at least two drives	Nonlinear curve fitting and parameter estimation program. It is particularly useful for solving problems in chemical kinetics.
CHEM Master Ver. 2.10, 2.10	Softtouch Envirogenics Langhorne, PA	IBM-PC/XT, PC/AT, 640 kb RAM with 540 kb free RAM	Right to know data base program. It might be helpful in maintaining information on hazardous chemicals, keeping track of the use of those chemicals and prepare community and worker right-to-know reports.
EPI Code, Ver. 4.1	Homann Associates, Inc. Fremont, CA	IBM-PC, PC/XT, PC/AT, or compatibles	A Gaussian model for evaluating the atmospheric dispersion of wide range of chemical releases. It was designed to provide quick estimates of downwind concentrations and can run on a minimal IBM compatible personal computer system.
Audit Master, Ver. 3.02	Utilicom, Inc. Pittsford, NY	IBM-PC, PC/XT, PC/AT, 512 kb RAM	Audit Master is a modular computer program that assists you in conducting health, safety, and environmental audits, to determine if operations and practices comply with applicable regulations.

(Continued on page A12)

(Continued from previous page)

Chemtox Database Release 1	Resource Consultants Inc. Brentwood, Tennessee	IBM-PC, PC/XT, PC/AT, 512 kb RAM. At least one 5 1/4" or 3 1/2" double sided diskette drive. 10 MB free space on hard disk.	This program is very useful when one wants to access a comprehensive information reference for toxic sub- stances. It functions much like a technical reference li- brary, with information on physical properties, toxico- logical information, regula- tory requirements, emergency response, personnel protec- tion, and much more.
Map Viewer, Ver. 1.0	Golden Software, Inc. Golden, Colorado	80286 & higher processor, windows 3.0 and higher, hard disk with 3 MB free space	Map viewer is a graphics program to create maps to communicate info. for spe- cific geographic areas.
Reg-A-Dex, Ver. 2.4	J. J. Keller & Associates Inc., Neenah, Wisconsin	IBM-PC, PC/XT, PC/AT, 1 MB free space on hard disk	Reg-A-Dex is a chemical re- gulation data base which al- lows you to quickly deter- mine whether a substance ap- pears on any one of several regulatory lists, such as SARA, RCRA lists.
Environmental Series Infobase	Legislative Information Systems Corporation Annandale, VA	IBM-PC, PC/XT, PC/AT & compat. 512 kb RAM	Environmental regulation in- formation data base main- tains 18 volumes of the federal "Code of Federal Regulations" in computer- readable "information" and distributes quarterly and monthly updates based on actions published in the "federal register." The en- vironmental series infobase must be used in conjunction with views by Folio (or pre- views, its runtime version)
Graftool, Ver. 3.3	3-D Visions, Inc. Redondo Beach, CA	IBM-PC, PC/AT, PC/XT, DOS Ver. 3.0 and higher, 2 MB free on hard disk	Technical graphics
OAQPS Technology Transfer Network Bulletin Board	U.S. EPA	Access to a PC modem, and communication software	Computer bulletin board, which provides access to info. regarding federal air quality regulatory programs, documents, data bases, and software tools.
Map Info. for windows Ver. 1.1	Map Info. Corporation Troy, NY	IBM PC/AT, PS/2 or com- patible, 2 MB RAM	This is a geographic informa- tion system. It might be helpful when working with large amounts of data and need to visualize and analyze those data graphically.

note: IBM-PC in this table implies all IBM-PC's and compatibles

- (d) **Research Software:** This category includes software originated from universities and research institutions. A review of journals will give you an idea on the type of software developed. Generally, you will have to contact researchers to find out about the availability of software. Some of the software developed at these institutions will appear as commercial software at a later date.
- (e) **Commercial Software:** There is a tremendous growth in the development of environmental software by consulting companies in the U.S., Canada and Europe. Advertisements appearing in trade journals and magazines and promotions during pollution conferences will assist you in locating the right software for your plant.
- (f) **Electronic Bulletin Boards:** These are inexpensive sources of obtaining pollution software. A paper

Table 2 Examples of software articles published in Environmental Progress during 1989-92

<u>TITLE</u>	<u>VOLUME/NO.</u>	<u>DESCRIPTION</u>
PC-SARA: A Software for Emergency Planning and Analysis	Vol. 8, No. 2	PC-SARA is a software developed by Technology and Management Systems, Inc., Burlington, BA, for emergency planning and analysis. It is designed to help industries and local communities in the U.S. comply with many of the requirements of SARA Title III.
WHAZAN: A Software for Chemical Hazard Analysis	Vol. 8, No. 3	The WHAZAN (World Bank Hazard Analysis) was developed by Technica International, Fullerton, CA. It can be used during an emergency involving chemicals to calculate and predict the concentration as a result of a chemical release.
HWI: A Software for Hazardous Waste Incinerators	Vol. 8, No. 4	HWI, developed by Professors Theodore and Reynolds from Chemical Engineering Department, Manhattan College, Riverdale, NY, assists in the preliminary design and analysis of incinerators.
TEST AIR: A Program for Air Pollution Testing Methods	Vol. 9, No. 1	The procedure used in the program is in accordance with the calculations given in the Title 40 of the Code Reference of Federal Regulations (United States of America), part 60, Appendix A (40 CFR 60, Appendix A). Help is available from Dawn Graphics, Winchester, MA.
The use of TK Solver for Environmental Engineering Problems	Vol. 9, No. 2	This software, developed by Universal Technical Systems Inc., Rockford, IL, helps environmental scientists/engineers in industry, regulatory bodies or universities in solving problems which involve equations (algebraic as well as differential) consuming lot of time.
An Indoor Air Quality Model	Vol. 9, No. 3	IAQ (Indoor Air Quality) model by Dr. Leslie E. Sparks of Air and Energy Engineering Research Laboratory of the U.S.E.P.A., NC, estimates the impact of various pollutant sources on indoor air quality.
Software for Regulatory Compliance of Chemical Hazards	Vol. 9, No. 4	This article briefly describes the available software for managing chemical hazards. They are grouped into six categories.
Use of Bulletin Board Systems for Air Quality Modeling	Vol. 10, No. 1	This article reviews about the available software programs related to air quality modeling from bulletin board systems like SCRAM, NTIS, etc.
Software to Study Environmental Effects of Hazardous Waste Sites	Vol. 10, No. 2	The software for hazardous waste sites are grouped into five categories and are discussed in this article.
Use of Electronic Bulletin Boards for Environmental Management	Vol. 10, No. 3	This article gives a brief description of the available 9 Bulletin Board Systems.
A Review of Three Toxic Release Screening Models	Vol. 11, No. 1	This article gives a brief description about the models TSCREEN, ARCHIE, and CAMEO which are widely used in the U.S. The sources and the cost of obtaining each model is also listed in the article.
Environmental Data Bases	Vol. 11, No. 2	Available popular data bases, their use, and the contact address to acquire them are briefly discussed in this article. Data bases concerned to air are of prime focus in this article.

by Kumar and Rao [4] provides information on some of the electronic bulletin boards available to you. They allow you to download pollution software, emission data, monitoring data, and regulatory information at your convenience.

(g) Newsletters:

Newsletters published by the California Air Resources Board (P.O. Box 2815, Sacramento, CA 95812), The European Association for the Science of Air Pollution (available from Prof. P. J. H. Builtjes, MT-TNO, P.O. Box 342, 7300 AH Apel-

Table 3 Examples of software cited in Environmental Software Report of Donley Technology

RISK * ASSISTANT

Developed by Hampshire Research Institute

Distributed by Thistle Publishing, Alexandria, VA

Purpose:

To assess chemical exposures and risks at specific sites. It allows users to rapidly evaluate exposures to, and human health risks from, chemicals in the environment, and to present the results in the form of detailed reports.

Hardware/Software Requirements

Runs on IBM/compatible microcomputers

RAM Required

512 K

Hard-disk Memory

5 Mb

Operating System

DOS 2.0 or greater

Other Requirements

an 80 column printer

Cost

\$199.95 (according to November, 1991 issue)

Technical support, database updates, and user bulletin board available at the developer.

VOC-CALC

Developed by Air Quality Consultants, Inc.

Diamond Bar, CA

Purpose:

To keep daily records of VOC's emitted into the atmosphere from their facility. It tracks VOC emissions by permit, equipment, and product according to the South Coast Air Quality Management District (SCAQMD) requirements.

Hardware/Software Requirements

Runs on IBM/Compatible microcomputers

Diskettes: 5 1/4" or 3 1/2"

Hard-disk Memory

4 Mb

RAM required

640 Kb

Operating System

DOS 2.0 or greater

Language written in:

Clipper

Cost

\$1,495 (according to November, 1991 issue)

Free demo available: technical support, users manual, and training available at the developer.

doorn, The Netherlands), Donley Technology's Environmental Software Report, and major consulting companies are also useful for learning about software and the modification in software. For example, the programs RISK * ASSISTANT and VOC-CALC are listed in Table 3, which are taken from Donley Technology's Environmental Software report, November 1991.

- (h) **Book Publishers:** Book Publishers are also entering into the lucrative market of pollution software. They are packaging the software and user's guide like a book. For example, Lewis Publishers announced the availability of Atmospheric Oxidation Rate Program, Biodegradation Probability Program, and Hydrolysis Rate Program in 1992.
- (i) **Information Database:** A search through information database is also helpful in locating software. For example, AIRBASE database is maintained by Air Infil-

tration and Ventilation Centre, University of Warwick Science Park, Coventry, U.K.

CONCLUDING REMARKS

Information on environmental software is scattered throughout the literature. Over 3,000 environmental software are available from the sources listed in this article. However, there is not a single source to obtain details on all the available software. It is hoped that the information presented will be helpful in your search for a software.

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Evolution of the Superfund Remedy Selection Process, Including an Assessment of Implementation of Permanent and Alternative Remedial Technologies

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The history of the Superfund program has been controversial, especially with respect to the development of the remedy selection process. During the early 1980's, USEPA rarely selected permanent remedies or alternative treatment technologies, relying on disposal and/or containment remedies. Dissatisfaction with the pace and extent of cleanup of the Nation's hazardous waste sites resulted in public and political pressure to address this situation. In response, USEPA's selection of alternative remedial technologies accelerated somewhat during the mid 1980's. At the same time, the original Superfund law and key regulations were being overhauled, culminating in enactment of the Superfund Amendments and Reauthorization Act (SARA) in late 1986. SARA emphasized selection of permanent remedies and alternative remedial technologies that treat a site's contaminated source materials. SARA also established the Superfund Innovative Technology Evaluation (SITE) program to evaluate alternative remedial technologies. Since SARA, USEPA claims continued acceleration in the selection of permanent remedies and alternative technologies, while critics question the permanence of many of EPA's selected remedies.

INTRODUCTION

In general, there are two kinds of technological innovations: i) innovations driven by the pursuit of scientific knowledge, without regard for possible applications, and ii) innovations driven by public and/or political demands to solve newly perceived problems. In the former, applications are viewed as secondary to the advancement of knowledge, while in the latter, the application of existing technology to new problems constitutes innovation, in and of itself.

In the field of hazardous waste site cleanup, most technological innovations have been of the latter kind, that is, application of existing technologies to newly perceived problems, in response to public and political demands. The use of any permanent or alternative treatment technology has been considered to be an example of "technological innovation" (which is different, however, from "innovative alternative technology", as defined under Superfund). Technological innovations are necessary but not sufficient to effect the remediation of hazardous wastes and hazardous waste sites. Political will and an effective regulatory framework are also required, to spur technology development and implementation.

REMEDY SELECTION UNDER SUPERFUND

Evolution of CERCLA/SARA

The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) became law in December 1980 [1]. In enacting CERCLA, Congress had two basic goals: (i) to effect cleanup of abandoned/uncontrolled hazardous waste sites and (ii) to ensure that the parties responsible for creating these problems would bear the response costs [2]. To implement CERCLA, Congress provided a "Superfund" of \$1.6 billion over five years. The Superfund, generated largely from taxes on the petroleum and chemical industries, was to be used when Responsible Parties (RPs) refused or were unable to pay for or perform site cleanups, or when no responsible parties could be identified. At the time, it was hoped that this program would be sufficient to repair the damage from careless hazardous waste disposal [3].

The cornerstone of CERCLA was a provision to revise and amend the National Contingency Plan (NCP), issued under Section 311 of the Clean Water Act for emergency cleanup of oil spills. The revised NCP was supposed to specify criteria for hazardous waste site identification, investigation and prioritization, and provides technical criteria for cleanup. As part of the NCP, EPA was instructed to develop a National Priority List (NPL) of at least 400 of the Nation's worst sites to be eligible for Superfund monies. The focus of CERCLA is remediation of these NPL sites, although CERCLA also contains provisions for emergency removal actions at non-NPL sites.

Promulgation of a revised NCP was necessary before EPA could begin a full-scale cleanup program. Delays in establishing a new NCP, as well as the unexpectedly slow obligation of Superfund revenues for emergency and remedial response actions, led to the resignations of EPA Administrator Burford and several of her appointed staff in February 1983 [4]. EPA published the revised NCP in July 1982 [5].

By 1985, it had become apparent that the extent of the hazardous waste site problem was much greater than originally anticipated. EPA estimated 2,000 eventual NPL sites [6], while the Office of Technology Assessment (OTA) estimated 10,000 eventual NPL sites [7]. The time and expense of remediating all of these sites were vast; estimates varied between 5 and 100 years at a cost of between \$5 billion and \$100 billion [7]. Furthermore, the pace of site cleanups was far below original expectations; at the end of 1984, EPA considered cleanup actions to be completed at only 10 of the 538 sites on the NPL [8]. The effectiveness of site removal and remedial actions was dubious; in general, wastes were excavated from one site and land-disposed at another or were contained on-site [7], even though most land disposal/containment facilities were expected to fail eventually [9].

In March 1985, Congress began discussion of CERCLA reauthorization, eventually leading to passage of the Superfund Amendments and Reauthorization Act (SARA) [10], in October 1986. Congress greatly reduced EPA discretion under SARA, especially in the area of site cleanup criteria [11, 12]. SARA cleanup standards, the 1990 revisions to the NCP, and the EPA Superfund Innovative Technology Evaluation (SITE) program have had a significant impact on hazardous waste site remediation, especially with respect to the selection of permanent and/or alternative cleanup technologies. In addition, SARA authorized an expanded \$8.5 billion Superfund, over its 5-year authorization period, for hazardous site cleanups, reflecting the knowledge that the hazardous waste site problem was much larger than originally expected.

SARA Cleanup Standards

The 1980 Statute and the 1982 NCP did not specify any particular cleanup standards; these criteria were left largely to

the discretion of EPA. The NCP simply stated that a selected remedy should represent the lowest cost alternative that effectively protects public health, welfare and the environment. The lack of clearly defined cleanup standards led EPA to frequently select "inexpensive", impermanent remedies, such as off-site disposal and on-site containment [7].

SARA Section 121, entitled "Cleanup Standards", establishes requirements governing selection of remedies at NPL sites, specifying that the President select remedial actions that are protective of human health and the environment, cost-effective, in accordance with the rest of Section 121, and in accordance with the NCP. In evaluating cost-effectiveness, both short and long-term costs must be taken into account. These requirements do not seem different from those in CERCLA and the 1982 NCP; however, the rest of Section 121 marks a major policy departure regarding site cleanups.

Two basic principles governing remedial action selection are contained in Section 121(b). The first is that permanent treatment is strongly preferred over land disposal and containment. SARA states that, "Remedial actions in which treatment which permanently and significantly reduces the volume, toxicity or mobility of the hazardous substances, pollutants, and contaminants is a principal element, are to be preferred over remedial actions not involving such treatment." The phrase "actions not involving such treatment" refers to land disposal and/or containment actions. Section 121(b) also states that remedial actions shall "utilize permanent solutions and alternative technologies to the maximum extent practicable". How this statement is interpreted and implemented (via the NCP) by EPA directly influences the use of permanent and alternative treatment technologies at Superfund sites.

The second principle is that "off-site transport and disposal" of hazardous materials should be the "least favored alternative remedial action where practicable treatment technologies are available". This bias against off-site disposal is strengthened by Section 121(b) (2) which allows selection of an "alternative" remedial action even if never utilized at any other similar site. This seems to be an attempt to circumvent the situation associated with most "alternative" technologies, that is, a technology cannot be used unless it has been "proven"; "alternative" technologies are "unproven"; therefore, "alternative" technologies cannot be used.

Congress did not specifically define language such as "permanent", "alternative", "maximum" extent practicable", "significantly reduces...", etc., to the degree necessary to determine the "best" remediation schemes for particular sets of circumstances. However, Congress' general intent was clear: stop moving the wastes from site to site and actually start cleaning these sites up. Programmatic details were left for EPA to develop in a revised NCP.

Section 121(d) contains provisions for determining the degree of cleanup for a selected remedial action to protect human health and the environment. It provides, for hazardous substances remaining on-site, the remedial action selected must attain "legally applicable or relevant and appropriate Federal and State standards, requirements, criteria or limitations" (ARARs). In particular, cleanups "shall at least attain Maximum Contaminant Level Goals (MCLGs) established under the Safe Drinking Water Act and water quality criteria established under Section 303 or 304 of the Clean Water Act", if relevant and appropriate. Establishment of uniform cleanup standards, such as ARARs, was Congress' attempt to provide a nationally consistent "how clean is clean" policy.

Finally, section 121(e) provides that "No Federal, State or local permit shall be required for the portion of any removal or remedial action conducted entirely on-site". This resolved a long-standing controversy [12] and encourages utilization of a greater diversity of remedial technologies, a least on-site. No permit exemptions for off-site treatment are made, strengthening the position against off-site remedies.

The Remedy Selection Process and Criteria

The remedial process, detailed briefly next, has not changed much over the years, but the evaluation criteria for some of the steps have changed substantially, reflecting SARA and the evolving NCP. After a site is placed on the National Priorities List, a Remedial Investigation and Feasibility Study (RI/FS) is carried out to delineate site contamination and risks to human health and the environment, and to evaluate candidate remedial alternatives. Then, EPA issues a Record of Decision (ROD) detailing the selected remedy and the Agency's selection rationale. After issuing the ROD, a Remedial Design (RD) study is performed to provide engineering and construction details for the remedy. Finally, Remedial Action (RA) commences. Some remedies require long-term monitoring to determine remedy effectiveness, and occasionally a ROD may be reopened and amended. When a cleanup is considered complete, the site can be delisted from the NPL.

SARA (Section 105) directed EPA to revise and republish the NCP by April 1988. The proposed NCP revisions were published in December 1988 and EPA promulgated the revised NCP in 1990 [14]. The revised NCP describes how EPA intends to implement the policy mandated by SARA. Prior to the revised NCP, the only guidance published by EPA regarding site cleanups was a July 1987 interim guidance, outlining nine key cleanup criteria [15]. The document did not rank these criteria; all appeared to have equal weight.

Section 300.430, Remedial Investigation/Feasibility Study (RI/FS) and Selection of Remedy, is the heart of the NCP, with respect to selection of remedial technologies. In general, the RI characterizes the site and its risks, while the FS establishes remedial action objectives, and develops and evaluates a range of remedial alternatives. This range should include alternatives that completely destroy all hazardous substances to the maximum extent feasible, as well as alternatives employing permanent treatment that reduces the toxicity, mobility or volume of hazardous substances to varying degrees.

The last step of an FS is a detailed comparison of alternatives with respect to a number of evaluation criteria. The 1990 NCP specifies nine criteria (similar to the nine criteria outlined in the 1987 interim guidance), that encompass statutory requirements and include other gauges of overall feasibility and acceptability. The nine evaluation criteria are organized into two "threshold criteria", five "primary balancing criteria" and two "modifying criteria". The two threshold criteria must be satisfied, and include i) overall protection of human health and the environment, and ii) compliance with ARARs. The five "primary balancing criteria" are used to compare and rank remedial alternatives and include: i) long-term effectiveness and permanence; ii) reduction of toxicity, mobility or volume; iii) short-term effectiveness; iv) implementability; v) cost. The two "modifying criteria" are i) State acceptance, and ii) community acceptance, and can prove to be as important to remedy selection as the technical criteria.

The 1990 NCP implies a more structured comparison of remedial alternatives than the 1987 Guidance or previous versions of the NCP. However, the "threshold criteria" are simply restatements of SARA's statutory requirements, and since no "weighting factors" are provided for ranking remedial alternatives with respect to the "primary balancing criteria", substantial Agency discretion appears to have been preserved. This is especially true with respect to the statutory provision to utilize permanent treatment to the maximum extent practicable—if this provision is not satisfied, EPA need only explain why in the ROD. In essence, EPA is only required to consider a range of permanent treatment technologies, and at least one innovative treatment technology, in addition to the usual disposal, containment and no-action alternatives.

It should be noted that in the 1990 NCP, EPA calls for the use of MCLs, instead of the more stringent MCLGs (maximum

contaminant level goals) specified in SARA. Some think EPA by-passed SARA by using the less protective MCLs [15]. However, former Assistant Administrator Porter has said, "If EPA puts out a standard (MCLs are EPA's applicable drinking water standards) for 200 million people to drink, can I really tell 10 people living next to a Superfund site that it's a different number for them? [16]." This statement has merit, especially when achieving some of the MCLGs (many of which are zero) would be exorbitantly expensive.

The SITE Program

In response to reports that Superfund site remediations rarely used permanent or alternative technologies [7, 8, 17], Congress provided for a research, development and demonstration program when reauthorizing CERCLA. SARA specifies that ten field demonstration projects of alternative or innovative treatment technologies are to be conducted each year, providing \$20,000,000 annually to fund EPA supervision and quality assurance efforts, and to fund up to 50% of the demonstration project, if warranted.

As a result of SARA's mandate, EPA developed the Superfund Innovative Technology Evaluation, or SITE, Program. The general goal of the SITE program is to "enhance the development and demonstration, and thereby establish the commercial availability, of innovative technologies at Superfund sites as alternatives to the containment systems presently in use" [18]. The SITE Program aims to achieve this goal by identifying impediments to the development and commercialization of alternative technologies and, if possible, removing these impediments by conducting alternative technology demonstrations, and developing procedures and policies to encourage selection of these alternative remedies at Superfund sites.

The SITE Program Manual [18], drawing from work done in previous impediment studies [7, 19, 20], identifies three primary categories of impediments to the acceptance and use of innovative alternative technologies. These are informational, regulatory and institutional impediments. Informational impediments include lack of adequate performance and cost data regarding specific technologies and uncertainty regarding the existence and size of the market for innovative technologies. A major focus of the SITE Program is to generate the data needed to address these informational impediments. Regulatory barriers include EPA's complex procurement procedures and the co-existence of different Federal, State and local environmental programs; the latter creates uncertainties regarding issues such as permitting and delisting. The SITE Program does not directly address regulatory impediments, because these impediments do not affect SITE demonstrations.

Institutional impediments include i) private party liability concerns, especially considering the uncertain nature of innovative technology performance; ii) governmental necessity for fund-balancing, as SARA's \$8.5 billion covers only a fraction of eventual cleanup costs; iii) community preferences for complete removal of hazardous wastes from nearby sites—the "OOMBY" (out of my backyard) syndrome; and iv) minimal involvement of academic and non-profit institutions, as these institutions are limited by SARA's 50% funding limit for SITE demonstrations. SARA addresses SITE Program private party liability concerns by allowing for some contractor indemnification during SITE demonstrations. The SITE Program also addresses community concerns through efforts to keep the public informed and allay public fears concerning innovative technologies. Non-technical issues, such as local politics and media coverage, can often influence remedial selections more than any technical issues. The other institutional impediments discussed are not addressed by SARA or the SITE Program.

Permanent, Alternative and Innovative Technologies Defined

Before assessing whether and how the use of permanent and alternative or innovative technologies has changed since SARA and the SITE Program, it is important to discuss how SARA and SITE define the terms "permanent", "alternative" and "innovative". SARA Section 121(b) (cleanup standards) does not define the difference between "permanent solutions" and "alternative treatment technologies"; however, it would not make sense to use both terms if there were no difference. The answer may lie in SARA Section 311(b) [10]; the terms "alternative or innovative technologies" are defined as "those technologies, including proprietary or patented methods, which permanently alter the composition of hazardous waste through chemical, biological, or physical means so as to significantly reduce the toxicity, mobility or volume of the hazardous waste or contaminated materials being treated" (emphasis added).

The underlined phrase distinguishes alternative or innovative (which are equated, here) technologies from permanent remedies. Permanent remedies are those that "significantly reduce toxicity, mobility or volume...", while alternative or innovative technologies are those that "significantly reduce toxicity, mobility or volume...by altering the composition of the hazardous wastes". This implies that, under SARA, alternative or innovative technologies are a subset of possible permanent remedies. For example, a containment technology can be seen as "permanent" if it reduces the mobility of contaminants, although many argue that containment can never be truly "permanent"; however, containment cannot be viewed as alternative or innovative, since the contaminated source materials, or wastes, are not altered. On the other hand, technologies such as solidification, which is considered to be a permanent and alternative (since it does "treat" the wastes) technology under the SARA and SITE definitions, is not considered by many to be a truly permanent remedy. Finally, SARA Sections 311(b) and 121(b) also imply that alternative or innovative technologies are not readily available, since they have not been demonstrated at a site or scale necessary for use at a Superfund site.

In the SITE Program, EPA seems to agree with these interpretations. The SITE Program categorizes three different levels of alternative technologies that "permanently alter the composition of hazardous wastes" [18]. The first category is available alternative technology. This is a technology, such as several forms of incineration and solidification/stabilization, that is in routine commercial or private use, especially if it qualifies under RCRA as a "best demonstrated available technology" for a particular waste stream. The second category is innovative alternative technology. This refers to a technology that is developed through the laboratory or pilot-scale, but requires full-scale testing to develop more complete cost and performance data before it is considered proven and available for routine use. The third category is emerging alternative technology. This refers to a technology that is in an early stage of development; the technology is conceptually promising, but has not passed laboratory or pilot-scale testing.

Remedial Technologies

Prior to evaluating remedial technologies, it is important to adequately define the nature and extent of site contamination, for example, what levels of which contaminants are present in particular media, and what risks do these contaminants pose to human health and the environment. Variations in contaminants, contaminant matrixes, and transport concentrations, and local human and ecological receptor patterns, make remediation of hazardous waste sites challenging and expensive. Integrated treatment process trains, consisting of several process steps, often are required to attain site cleanup goals. Since

site characteristics are variable, design and operation of treatment systems must be tied to specific site conditions; thus, it is difficult to transfer treatment processes from one site to another. Site variability is one of the primary reasons EPA has retained significant discretization in the remedy selection process.

A wide variety of physical, chemical, biological, thermal and fixation/stabilization technologies are potentially applicable to Superfund wastes [23, 24]. It should be kept in mind that metals can never be "destroyed", only separated, concentrated and possibly recovered or immobilized and disposed, whereas all organic species can be "destroyed", under the right conditions, being converted into harmless residuals. Most of these technologies have been used by the chemical and petrochemical industries for decades; use for hazardous waste remediation is "technologically innovative" because application for this purpose is novel. Since each of these technologies treats wastes, they are considered alternative technologies under SARA. Whether or not they are available or innovative alternative technologies (considering SITE definitions) depends on whether they have been demonstrated at full-scale at a Superfund site, or are in routine use elsewhere, for example, under RCRA (Resource Conservation and Recovery Act).

Physical treatment utilizes physical characteristics to effect separation or concentration of waste stream constituents, generally requiring further treatment to destroy/immobilize/recover the contaminants of interest. Chemical treatment employs chemical reactions to alter the chemical composition of contaminants, that is, to convert organic species into mineralized end-products, such as carbon dioxide, and to convert metals to less toxic forms, by changing redox state. Biological treatment employs microorganisms to degrade organic species to less toxic end-products, and can be aerobic, anaerobic or a serial combination of both. Thermal treatment employs high-temperature thermal destruction of organic matter; the most important thermal technologies are the various forms of incineration. Solidification technologies are either physical or chemical processes and are important enough to warrant a separate category. These technologies immobilize toxic constituents, usually contaminated soils or sludges. Long-term effectiveness of these technologies has not been proven [25], and this is a source of contention with respect to whether or not solidification remedies should be considered permanent.

REVIEW OF REMEDIES SELECTED UNDER SUPERFUND

Permanent and Alternative Technology Use: Introduction

It is difficult to distinguish between permanent remedies, and available alternative and innovative alternative technologies, and to quantify their use at Superfund sites. For the most part, these terms have not been distinguished by EPA and most reviewers; most reporters of the use of permanent remedies do not discuss whether these permanent remedies use alternative technologies (available or innovative) to treat contaminated source materials. The EPA Fiscal Year ROD Annual Reports [22] summarize use of permanent remedies at Superfund sites for particular years, but do not state whether these remedies use alternative technologies to treat the contaminated source materials and do not provide details on how data were generated.

Furthermore, although it is relatively easy to tally the use of alternative technologies over the years, it is far more difficult to determine whether the use of an alternative technology constitutes a permanent remedy for the following reasons: i) there are some alternative technologies, such as solidification, that many do not consider to be permanent remedies, ii) in many cases an alternative technology may only be applied to a small amount of a site's contaminated source materials, leaving the

permanence of the overall site remedy in question, and iii) many sites engender multiple RODs, pertaining to multiple operable units (discrete areas), complicating determination of remedial permanence. Therefore, it is easier to report which RODs use alternative remedial technologies, that is, those that treat contaminated source materials, and leave open the interpretation of whether the alternative technology used constitutes a permanent remedy.

Considering the preceding discussion, it is difficult to establish more than general trends regarding patterns in use of permanent and alternative technologies under Superfund. However, it is possible to delineate three significant periods in Superfund history with respect to remedy selection, corresponding to important milestones in the evolution of the Statute and the NCP. The first is 1980-1984, during which containment and offsite disposal were almost always the selected remedies. The second period is 1985-1986, during which the 1985 NCP was published and CERCLA was being reauthorized. During this period, the selection of alternative technologies increased, in response to public and Congressional pressure, and in anticipation of SARA directives. The third period is 1987 to the present, subsequent to SARA, during which the use of alternative technologies accelerated even further; however, the performance of these remedies is disputed, as will be discussed.

Table 1 summarizes RODs selecting alternative remedial technologies at Superfund sites through 1990 (some RODs selected multiple alternative technologies, but the ROD is only counted once for this table). This table summarizes data from the authors' review of every ROD abstract through 1990, updating the authors' previous review of ROD abstracts through 1988 [26]. Interestingly, EPA's Technology Innovation Office (TIO) recently performed a similar survey, and discrepancies between the authors' data and the TIO data are minor [27].

Technologies considered alternative for this table are either available alternative technologies or innovative alternative technologies. Available alternative technologies include incineration and solidification, while, in general, all other alternative technologies are considered innovative alternative technologies—these include soil washing, soil flushing, thermal desorption, in-situ and on-site bioremediation, vapor extraction, dechlorination, vitrification, wetlands application and waste recycling. The Table also includes estimates of the percentage of alternative technologies that could be considered available or innovative.

Permanent and Alternative Technology Use: 1980-1984

A review of the ROD abstracts for this period (see Table 1) indicates that 6 of 55 RODs (11%) selected alternative remedial technologies; the performance of these remedies is question-

able, as will be discussed. There were two in-depth reviews of remedy selection, by OTA [7] and GAO [17], for the period 1980-1984; in addition, EPA published a report [22]. During the early years of Superfund, containment and/or disposal or no-action were the remedies of choice. The GAO report states that: in 1982, 0 of 4 RODs selected permanent remedies; in 1983, 2 of 13 RODs selected permanent remedies; in 1984, 8 of 38 RODs selected permanent remedies (no RODs were signed in 1980 or 1981). Thus, according to GAO, permanent remedies were chosen in only 10 of 55 decisions in the first five years of Superfund. The OTA report presented similar findings, but the EPA report differed.

According to the GAO report [17], of the ten permanent remedies selected during this period, incineration was chosen three times, solidification was chosen three times, and groundwater pumping and treatment accounted for the other four permanent remedies. Under SARA and the SITE program, incineration and solidification would be considered examples of permanent, available alternative treatment technologies. They would be considered alternative in that they alter the composition of the hazardous substances. Further, they would be considered available (especially incineration), since they were in routine use by industry for RCRA hazardous wastes [28]. However, as has been discussed, many critics feel that solidification is not a permanent remedy as it only immobilizes the hazardous substances contained in source materials and should be termed enhanced containment. These data also show that no RODs selected innovative alternative technologies during this period.

There is also disagreement over whether groundwater pumping and treatment is either permanent or alternative. Unlike the GAO report [17], the 1987 EPA report [22] did not consider groundwater pumping followed by treatment to be a permanent remedy; thus, EPA took credit for permanent treatment remedies for only 6 of 55 RODs (11%) during this period. Interestingly, EPA seems to contradict itself in the 1991 TIO report [27], in which it considers groundwater pumping and treatment to be a permanent remedy, employing "source control", distinguishing these remedies from alternative technologies that treat contaminated source materials. However, none of the reports considers groundwater pumping and treatment to be an alternative technology since it only addresses control/col-lection of waste streams, not contaminated source materials. Note that, groundwater pumping and treatment should be distinguished from in-situ soil flushing followed by treatment, which directly addresses contaminated source materials, accelerating site cleanup relative to pumping and treatment.

Generally, the reports acknowledged that for the RODs counted as selecting permanent remedies only a small portion of the total cleanup was actually considered permanent. It is doubtful whether these remedies would satisfy the later SARA requirement for selecting permanent and alternative technologies to the maximum extent practicable. As an example, at the Burnt Fly Bog site in NJ, wastes in drums were to be incinerated off-site for \$50,000, while the rest of the site materials were to be excavated and disposed off-site at a cost of \$8,000,000. Even so, this site was given credit for selection of a permanent technology.

Permanent and Alternative Technology Use 1985-1986

The years 1985 and 1986 were transition years for the Superfund program, with respect to implementation of permanent and alternative technologies. Our review of the ROD abstracts indicates that in 1985, 17 of 70 RODs (24%) selected alternative treatment technologies for contaminated source materials and in 1986, 27 of 83 (33%) RODs did so. According to the 1991 EPA-TIO report [27], in 1985, 19 of 70 RODs (27%) selected alternative treatment technologies and in 1986, 27 of 83 (33%) RODs did so. Finally, the 1987 EPA report

Table 1 Selection of Alternative Remedial Technologies at Superfund Sites

Year	*RODs Selecting Alternative Tech	Total RODs	% RODs Selecting Alternative Tech
	1980-1984		6
1985	17	70	24%
1986	27	84	32%
1987	28	77	36%
1988	68	153	44%
1989	75	144	52%
1990	89	168	53%
Total	310	751	41%

*Of the 310 RODs selecting alternative technologies, ~42% selected innovative alternative technologies, and ~58% selected available alternative technologies (incin. or solid.)

[22] indicated that in 1985, 15 of 70 RODs (21%) selected permanent remedies and, in 1986, 27 of 83 (33%) RODs did so. [Remember that this report did not differentiate between permanent remedies and alternative technologies, although it is likely that the report refers to alternative technologies, since it did not include groundwater pumping and treatment as a kind of permanent remedy.] All of the these reports show marked improvement compared to 1980–1984, probably due to pressure resulting from general dissatisfaction with the cleanup record, coupled with the 1985 NCP revisions and Superfund reauthorization momentum.

It is important to note that great difficulty is involved in reporting the use of permanent and alternative treatment technologies, as well as comparing different reports in this area. For example, reference [13] claims that, in 1985, “some form of treatment” was used in seventy-one cases and, in 1986 “some form of treatment” was used in eighty-four cases. In this report, “some form of treatment” includes groundwater pumping and treatment, and multiple treatment units per site are included. These data might mistakenly lead to the conclusion that permanent remedies were being selected more frequently than was true.

For the 44 RODs selecting alternative treatment in 1985–1986 (17 in 1985 and 27 in 1986), incineration was chosen twenty times, solidification/stabilization was chosen thirteen times, soil aeration (to volatilize organics from the soil) was chosen seven times, soil flushing was chosen five times, and soil-based biodegradation was chosen two times. These total forty-seven because EPA selected multiple possible remedies for three RODs in 1986. Incineration and solidification would be considered available alternative technologies. However, soil aeration, soil flushing and soil-based biodegradation had never been used at a Superfund site and were not in routine use by industry. Using SITE Program definitions, the latter are examples of the use of innovative alternative technologies; thus innovative alternative technologies accounted for 29% of the alternative technologies selected.

One hundred-five RODs signed during 1985–1986 did not select alternative treatment technologies. No-action, off-site disposal, and on-site containment were the principal remedies selected; about half of these RODs employed some form of groundwater pumping and treatment, to prevent off-site migration of contaminants at the site [17]. While in 1980–1984 most of the RODs selecting alternative treatment selected it to clean up only a small portion of site, for 1985–1986, the alternative technologies selected addressed significantly more contaminated materials than in 1980–1984 [12].

Permanent and Alternative Technology Use: 1987–1990

Starting with FY 1987, that is, October 1986, all RODs were to be performed in accordance with SARA, which was enacted in October 1986. As discussed, SARA directs EPA to favor the selection of permanent treatment technologies over land disposal and containment, and to select permanent and alternative treatment technologies to the maximum extent practicable.

A review of the ROD abstracts during this period (see Table 1) shows a continued increase in selection of alternative technologies: in 1987, 28 of 87 RODs (36%) selected alternative treatment technologies for contaminated source materials; in 1988, 68 of 153 RODs (44%) selected alternative treatment technologies; in 1989, 75 of 144 RODs (52%) selected alternative treatment technologies, and in 1990, 89 of 168 RODs (53%) selected alternative treatment technologies. Overall, 260 of 542 RODs (48%) selected alternative treatment technologies during this period. These figures are within a few percent of those in the 1991 EPA-TIO report [27]. Once again, of the RODs not selecting alternative technologies, most selected no action, offsite disposal or on-site containment; many of these also selected groundwater pumping and treatment.

Of the 260 RODs during this period that selected alternative treatment technologies, close to 50% selected innovative alternative technologies. This represents a significant increase in the use of innovative alternative technologies relative to the period prior to SARA and the SITE Program. Innovative alternative technologies selected included soil washing, soil flushing, thermal desorption, *in-situ* and on-site bioremediation, vapor extraction, dechlorination, vitrification, wetlands application and waste recycling. The remaining alternative treatment RODs selected available treatment technologies—incineration and solidification.

When does an innovative technology become an available alternative technology—is it after the remedial action is completed, or only after the technology has been in operation long enough to generate reliable data? At this point, soil aeration, soil flushing and soil-based degradation, in particular, would probably still be considered innovative alternative technologies, even though they were selected at other sites, during 1985–1986. This is because the remedies at these sites have not been completed, and performance and cost data are still incomplete. Also, application of these technologies at Superfund sites has been much less extensive than application of incineration and solidification/stabilization technologies, which are generally considered as “available”. However, EPA still considers certain types of incineration and solidification/stabilization technologies to be at the innovative alternative technology development stage, since many variations of these technologies were accepted into the SITE demonstration program [27].

Since 72% of all RODs signed through 1990 were signed since SARA, this period is an especially important one in Superfund history. Although this review and EPA’s TIO report [27] show that nearly half of all RODs since SARA selected alternative treatment technologies, there is much disagreement over whether EPA actually fulfilled the mandate for permanent remedies. The report “Right Train, Wrong Track” (RTWT), published by a combination of environmental and industrial interests, is highly critical of EPA’s performance since SARA [15]. The report concludes that EPA has not fulfilled SARA mandates regarding permanent remedies and is continuing to rely primarily on disposal and containment remedies.

The RTWT report found that i) 68% of the remedies selected in FY 1987 failed to treat contaminated source materials; ii) 24% selected partial or ineffective treatment remedies; and, iii) only 8% used treatment technologies to the maximum extent practicable, as required by SARA. RTWT does not consider solidification/stabilization to be a permanent remedy, and it points to several remedies that only treated a small fraction of source materials that were credited as permanent. The report blames weak Federal management, especially continued use of cost and effectiveness as equal partners in the remedy selection process. The report concludes by saying that it is difficult to imagine a more specific or better funded statute than SARA, but that SARA cannot be made to work when EPA lacks the motivation to make it work.

Another report, OTA’s “Are We Cleaning Up?”, [29] echoes RTWT findings regarding selection of permanent remedies, since SARA. This report does not provide as broad a summary as RTWT, but focuses on ten detailed case studies to illustrate programmatic shortcomings. The case study of the Crystal City, Texas site illustrates some of these shortcomings.

At Crystal City, the selected remedy for soil contaminated with high concentrations of pesticides (including DDT) and metals was the excavation of the soils and disposal on-site in an unlined, capped landfill. The on-site landfill did not comply with applicable RCRA requirements for landfill design. No treatability study supported the conclusion that this remedy, based on adsorption and immobilization of the contaminants by site soil, was permanent. Permanent alternatives, such as incineration, soil washing/treatment, and thermal separation were rejected; according to OTA the reason was cost. This type of problem is common according to OTA. The primary

reasons for this are i) too much flexibility and lack of central management control; ii) emphasis on detailed results instead of evaluation of what the results accomplish; iii) lack of information regarding permanent technologies, focus on short-term costs; and, iv) Agency inability to hire and retain competent staff.

Given the discrepancies between the two reports just discussed [15, 29] and the EPA reports on the use of permanent and alternative technologies [22, 27], it is difficult to determine to what extent SARA directives have been satisfied. These discrepancies led to severe disagreement between EPA personnel and the authors of the two critical reports [30]. Reality probably lies somewhere between the divergent views presented. While it is unarguable that the use of alternative treatment technologies (both innovative and available) has greatly accelerated since SARA, it is probably true that the use of permanent remedies has improved since SARA, but not as much as EPA has claimed.

Finally, it is too early to tell what, if any, impact the 1990 revisions to the NCP have had on remedy selection. However, the 1987 interim guidance and the 1988 draft NCP anticipated the 1990 final NCP, and were probably partly responsible, in conjunction with the SARA statute itself and the SITE Program, for the acceleration in the consideration and selection of permanent and alternative remedies during this period.

Permanent and Alternative Technology Use: Other Considerations

Even if consistent and reliable cost and performance data were available for hazardous waste treatment technologies and EPA made a stronger effort to select permanent and alternative remedial technologies, increased use of these technologies would not be guaranteed. The primary reason is that permanent and alternative treatment remedies are more expensive than containment and monitoring remedies, and may not be feasible for thousands of Superfund sites. For the 1987 RODs selecting alternative treatment, the average estimated remedial costs were in excess of \$15,000,000 per site [22]. More recent estimates indicate an average remedial cost of \$30,000,000 per site [32].

As has been discussed, many of these remedies were not truly permanent remedies, which would have been even more expensive. Furthermore, the final number of NPL sites could be 10,000 or more [7], meaning it might eventually require \$300-\$700 billion to permanently clean up all of these sites. If funding were maintained at current levels, it would require decades to permanently remediate all Superfund sites. Worse yet, it has been estimated that it may eventually cost several hundred billion dollars for remediation of Federal waste sites from the Departments of Defense and Energy. Additionally, the future funding level for Superfund and Federal sites remediations cannot be predicted.

A recent GAO report [33] stated that "it is doubtful that the Superfund Program, as currently operated, will ever clean up all hazardous waste sites". It is not encouraging that after ten years and \$11 billion spent, EPA considers cleanup work to be completed at only 60 of the 1,200 NPL sites [32]. Finally, important regional and global environmental problems, such as ozone depletion, climate change, habitat destruction and resource depletion, have emerged over the last few years, lessening the relative importance of hazardous waste site cleanup in the eyes of many. The discussion above is not an argument against the use of permanent and alternative technologies, but rather an acknowledgement that EPA must better prioritize among remedial activities, as well as better prioritize remedial activities among the suite of other environmental problems demanding attention.

SITE Program Performance

Through 1991, the SITE Program has gone through six technology solicitations, and there are currently 58 technologies in the innovative alternative technology demonstration

program with 30 demonstrations completed [31]. For the SITE demonstration program, accepted technologies include innovative incinerator/thermal treatment technology designs, innovative solidification/stabilization technologies, innovative biological processes, innovative soil extraction/washing technologies, innovative soil aeration/vacuum extraction technologies, innovative physical separation technologies, and more. For the 30 field demonstrations completed at Superfund sites, about a dozen final reports have been released [31].

Results from the SITE Program indicate that most of these technology demonstrations have been successful in generating important baseline performance and cost data, and many have been successful in achieving desired remedial goals. Of the 58 technologies involved in the demonstration program, several have been selected as remedial technologies in about 14 subsequent RODs (some technologies have been selected multiple times) [31]. In addition, many more of these 58 technologies are under consideration for future RODs. Thus, it seems that the SITE Program has been reasonably successful in achieving its goals, especially given its modest funding; currently the SITE Program accounts for less than 1% of the Superfund budget; in contrast, most technological companies spend 5-10% of their budgets on research and development.

CONCLUSIONS

The Superfund remedy selection process has changed considerably over the history of the Superfund program, as reflected by trends in the selection of permanent remedies and alternative remedial technologies. There have been three significant periods in Superfund history with respect to remedy selection, corresponding to important milestones in the evolution of the Superfund statute and regulations. The first is 1980-1984, during which containment and offsite disposal were almost always the selected remedies; during this period, only 11% of 55 total RODs selected alternative treatment technologies. The second period is 1985-1986, during which the 1985 NCP was published and CERCLA was being reauthorized. During this period, the selection of alternative technologies increased to 29% of 154 total RODs, in response to public and Congressional pressure, and in anticipation of SARA directives. The third period is 1987 through 1990, subsequent to SARA, and during which the SITE program commenced, and the NCP was revised. During this period, the use of alternative technologies accelerated even further, to 48% of 542 total RODs. SARA (and the NCP) directives promoting consideration and selection of permanent remedies and alternative technologies, as well as the SITE Program's success in demonstrating alternative technologies, were instrumental in this acceleration. However, although acceleration in the selection of alternative technologies is indisputable, many critics have questioned the degree of performance of many of the remedies that employ alternative technologies.

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Critical Evaluation of PCB Remediation Technologies

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Polychlorinated biphenyls (PCBs) are a family of aromatic compounds consisting of a biphenyl molecule which has been chlorinated to form a large number of possible congeners. The number of chlorine atoms they can contain (from 1 to 10) varies, as does the placement of the chlorine atoms on the biphenyl molecule. Thus, a polychlorinated biphenyl is one of 209 compounds having the formula: $C_{12}H_{10-n}Cl_n$. Due to their excellent heat stability, fire retardance and electrical insulating properties, they gained widespread use as dielectric fluid incorporated in electrical transformers and capacitors. They were also incorporated in products as various as plastics, hydraulic fluids, surface coatings, inks, paints, pesticides, lubricants, and carbonless copy paper.

INTRODUCTION

From 1929 through 1980, the world production of PCBs was about 2.4 billion pounds. It is estimated that in the United States, about 404 million pounds of PCBs are still in use and accessible, about 262 million pounds are still in use and generally not accessible, and about 585 million pounds have been destroyed or are in storage, landfills, or the environment. The PCBs still in use and accessible are in transformers, capacitors, and other electrical equipment. Within the last category are PCBs in sediments, soil, vegetation and animals, the atmosphere, and fresh water totalling about 24 million pounds, another 13 million pounds are in the oceans, about 385 million pounds are in landfills and other storage, and an estimated 162 million pounds have been degraded.

In the mid 1960's, concerns regarding the toxicity and persistence of PCBs in the environment led to their eventual control in the United States under the Toxic Substances Control Act of 1976 (TSCA). TSCA regulates the manufacturing, processing, distribution in commerce and use of PCBs (40 CFR 761 et seq.). Subpart G of 40 CFR 761, the PCB Spill Cleanup Policy, specifies "how clean is clean" for spills of PCBs which occur after the effective date of the policy (May 4, 1987). The PCB Spill Cleanup Policy does not apply to several categories of spill situations, including historic spills (those which occurred prior to the policy's effective date), spills which directly contaminate or migrate into surface waters, sewers or sewer treatment systems, private or public drinking water sources or distribution systems, and spills which contaminate animal grazing lands or vegetable gardens. For spills which fall in any of these categories, a cleanup standard must be negotiated with the cognizant regulatory agency(s). Determination of an acceptable residual concentration is imperative prior to selecting a remedial technology for treatment of the specific waste stream(s).

The primary basis of establishing a cleanup standard is the protection of public health and the environment. However, the ability to reach a cleanup level in a given situation is also

considered. Thus, current knowledge of the capabilities of remedial technologies is vital. Development of PCB treatment technologies continues due to the ubiquitous nature of the chemical. This paper discusses the current state of development of the available technologies.

INCINERATION

Incineration is a recognized technique of PCB destruction. TSCA requires a "six-nines" (99.9999%) destruction and removal efficiency (DRE) of PCBs for thermal treatment systems. Therefore, for an incineration system to be permitted to destroy PCB containing wastes, it must be able to demonstrate conformance with this strict standard. The high temperatures and long residence times usually required to conform to this standard generally destroy all other organic components of the waste as well.

There are less than ten TSCA permitted commercial PCB incinerators currently operating in the United States. These vendors indicate that PCB destruction costs range from approximately \$500 to \$800 per ton for solid waste and \$3.25 to \$5.00 per gallon for liquid waste. Costs are dependent upon waste characteristics such as heating value and burn characteristic of the waste, PCB concentration, waste matrix, and total amount of waste treated, among other factors.

In some instances, it may be more economically feasible to bring a TSCA permitted incinerator to the waste, rather than transport the waste to a commercial incinerator. However, public acceptance of on-site incineration may be limited. Early regulatory agency and public involvement prior to selection of this remedial alternative may help alleviate the historical "NIMBY" (not in my backyard) attitude against thermal destruction units.

Transportable incinerators are comprised of the same unit operations as permanent, commercial facilities, namely: primary and secondary combustion chambers, feed systems, bot-

tom and fly ash handling units, air emissions control (filters, electrostatic precipitators, wet scrubbers), heat exchangers, and exhaust stacks. Waste water treatment for cooling/scrubbing water recycle/disposal and a mobile on-site laboratory can be integral supporting operations for transportable incineration systems.

Roy F. Weston, Inc., among others, operates a TSCA permitted Transportable Incineration System (TIS) which utilizes a 23 million BTU/hr rotary kiln as the primary combustion chamber. The kiln is of standard countercurrent cylindrical design which allows retention times of fifteen to ninety minutes. Operating temperatures can be varied below 1200 to 2200°F and the system can process from two to ten tons per hour of contaminated soils. It is also designed to be capable of incinerating fume, hazardous liquids and sludges at rates up to 233 million BTU/hr of heat release. A demonstration test performed in May 1988 indicated that the system could process an average of 13,650 lb/hr of soil spiked with PCB oil to an average concentration of 14,740 parts per million (ppm). The DREs achieved during this demonstration ranged from 99.99983% to 99.999990%, with residual PCB concentrations in the bottom ash of .01 ppm to .15 ppm.

The feed conveyor system requires a maximum particle size of two inches, therefore, materials handling must assure this limit can be met. For loose, sandy soil, simple screening can accomplish this end. Soils with high cohesion will require an operation, such as shredding, which will break down the feed to the appropriate size. As with all incineration systems, inorganic (heavy metal) constituents are not destroyed, but passed through to the ash streams. Stabilization of these streams may be required to immobilize the inorganic components to acceptable levels.

The TSCA permit granted to the TIS eliminates the need to get additional Federal TSCA permits as the unit is moved from site to site. However, National Pollutant Discharge Elimination System (NPDES), Publicly Owned Treatment Works (POTW) discharge, and/or air emissions permits may still be required. Additionally, if the waste feed can also be characterized as Resource Conservation and Recovery Act (RCRA) hazardous waste, a RCRA Treatment Storage and Disposal Facility (TSDF) permit must be gained.

The cost of remediating PCB contaminated soils via the TIS can range from \$140 to \$600 per ton; and generally fall in the \$180 to \$200 per ton range. These costs are mainly dependent on the heating value of the waste, the concentration of PCBs to be destroyed, and the total quantity of waste to be remediated.

Ogden Environmental Services owns and operates a transportable 10 million BTU/hr Circulating Bed Combustor (CBC). The CBC can provide DREs of 99.9999%, and is available for on-site operation. Soil feed rates vary based on soil moisture content and heating value of the waste. Solids, liquids and sludges may be treated utilizing this system, however, a maximum particle size of 1" for solid feed will determine the precombustion material preparation and handling requirements.

The thermal treatment unit of the CBC consists of ceramic lined combustion loop which is comprised of a combustion chamber and cyclone. Waste is fed into the loop along with limestone, which neutralizes acid gases formed during the thermal destruction reactions. The waste contacts hot recirculating soil from the cyclone. As it heats, it is entrained with air and travels upward through the combustor into the cyclone, where the solid fraction is separated from the combustion gases. The hot solids drop down to reenter the combustion chamber, where they will aid in heating new feed being introduced. Remediated solids remaining in the lower portion of the combustion chamber are removed at a controlled rate by an ash conveyor system.

Like the TIS, the CBC is TSCA permitted. However, air emissions, water discharge and RCRA permits must be ob-

tained as required. Treatment costs for remediating soils by CBC typically range from \$100 to \$300 per ton, depending primarily on soil moisture and quantity of material to be processed.

Westinghouse Environmental Services has developed and markets a Pyroplasma plasma arc process which utilizes a plasma torch to pyrolyze liquid organic materials at temperatures up to 15,000°C. Throughput capacities vary from one to three gallons per minute in single stage units. Waste liquids are aspirated into a superheated gas stream, where the molecular bonds of the waste are broken into their component atoms. These atoms recombine in the reaction chamber to form non-hazardous gases such as carbon monoxide, nitrogen, hydrogen, and some low molecular weight hydrocarbons. Acid gases and particulate carbon are removed in a wet scrubber. The resultant gaseous stream, primarily hydrogen and carbon monoxide, is drawn off and flared.

The Pyroplasma unit is suitable for liquid wastes only. Under a TSCA Research and Development Permit, it has demonstrated DREs greater than 99.9999% for PCB liquids with concentrations of 70-80% PCBs by weight. This technology is available in mobile units. Permitting and public acceptance issues for this treatment system are the same as those for the TIS and CBC.

A transportable Infrared Incineration System has been designed by Shirco Infrared Systems, Inc., which utilizes electrically powered silicon carbide rods to provide infrared energy that heats organic waste to combustion temperatures. Remaining combustibles are incinerated in an afterburner. A demonstration of this system in 1987 under the United States Environmental Protection Agency's (EPA's) Superfund Innovative Technology Evaluation (SITE) program demonstrated its ability to destroy PCBs at concentrations ranging from 10 ppm to 669 ppm in the feed with DREs exceeding 99.99%. While this demonstration did not meet TSCA's requirement for PCB destruction by thermal treatment, other tests with the same unit have achieved DREs of 99.9999%. Therefore, this incineration system, based on waste specific trial burn results, may be granted TSCA approval for remediation of PCB contaminated soils.

IN-SITU VITRIFICATION

A variation of traditional thermal treatment systems in the In-Situ Vitrification (ISV) Technology developed by the Pacific Northwest Laboratories Division of Battelle Memorial Institute and marketed exclusively by Geosafe Corporation. ISV is a process which melts inorganic soil for the purpose of thermally destroying its organic component. This is accomplished as follows.

Electrodes are placed in the soil to the desired treatment depth. A conductive starter path is placed on the surface between electrodes, and the treatment area is covered by an off-gas collection hood. As a result of the electric potential between the electrodes, current which flows through the starter path generates heat which in turn melts the underlying soils. The molten soils are generally quite electrically conductive, allowing the process to continue to depth. The high temperatures within the molten soil cause organic material (either naturally occurring or contaminants) to volatilize and pyrolyze. The resultant gases either become dissolved in the melt or move to the surface, where they combust on contact with air. Products of pyrolyzation and combustion are collected in the off-gas collection hood, and are treated prior to emission.

As the soils melt, the void space is removed. A volume reduction of 20-40% is typical. When the melt mass reaches an optimum, power to the electrodes is removed and the soil is allowed to cool naturally. As it cools, it vitrifies into a monolith which resembles naturally occurring obsidian (vol-

canic glass). The surface depression which results from the reduction in volume may be backfilled with clean soils, allowing for unrestricted future use of the area upon approval by the cognizant regulatory agency.

Potentially toxic inorganic contaminants are chemically incorporated in this matrix. Leach, hydration, and weathering tests of vitrified waste indicate that it has excellent long-term stability and can expect a mean life of thousands of years.

The vendor indicates this process exceeds PCB DREs of 99.9999% as required by TSCA, but requires treatability testing on actual waste samples to verify the process is capable of satisfying cleanup requirements. They also indicate this method is applicable to a variety of organic, inorganic and radioactive materials.

The ISV process is an in-situ treatment, and the treated vitrified waste may be left in place. As such, materials handling requirements are minimized. While the process can operate in fully saturated soils, the energy required to vaporize water could more cost effectively be used in vitrifying soils. Organic and inorganic debris may be left in place and treated within the melt volume, dependent on their expected effect on off-gas generation and residual product.

This technology is commercially available through Geosafe, which holds worldwide exclusive rights to it. Costs for utilizing this technology are on a similar order of magnitude as incineration, but can vary greatly based on variables such as waste-soil properties, volume of material, depth of required vitrification, unit price of electricity, moisture content, and distance of the site from the vendor's base location in Washington.

DESTRUCTION USING QUICKLIME

At several EPA remedial action sites in the recent past, observations by regional staff had suggested that treatment with quicklime (CaO) may achieve destruction of PCB contaminated soils and sludges.

EPA's Risk Reduction Engineering Laboratory (RREL) initiated studies, both in-house and through a contracted laboratory (RMC Environmental and Analytical Laboratories) to verify the results indicated in the field. The initial study conducted by RMC were extremely limited in scope, and indicated that reductions in PCB concentrations, on the order of 90%, were achieved in the waste matrices. The in-house project designed by RREL and conducted by their on-site contractor, Technology Applications Inc., indicated that the reductions detected in the waste matrices were due to evaporation and steam stripping in PCBs during the lime shaking process. Furthermore, only minimal amounts of products of phenyl-phenyl bond cleavage were detected, further supporting the theory that this process is not applicable to the destruction of PCBs.

BIOREMEDIATION

Biological treatment technologies use microorganisms to detoxify or decompose degradable organics. Naturally occurring (native) species may be utilized or specially adapted microorganisms may be introduced into the contaminated media.

Biodegradation of PCBs as a remedial technology is in the developmental stages. Many studies have identified several microbes which exhibit an ability to degrade specific PCB congeners to varying degrees. These microorganisms include several species of *Achromobacter*, *Alcaligenes*, and *Pseudomonas*, as well as a fungus, *Phanerochaete chrysosporium*. Best results can be obtained in biological reactors which can insure the necessary aeration, mixing, temperature control and nutrient delivery to optimize the biokinetics.

Biological treatment systems are living systems. Survival of the necessary microbes is vital for this technology to be feasible. It is therefore necessary to conduct treatability testing on actual waste samples to determine if the microorganisms can degrade the specific PCB congeners present or even survive.

While the inherent toxicity of PCBs indicates that their biodegradation would occur only at dilute concentrations, laboratory studies performed by General Electric Company, Corporate Research and Development have indicated degradation of soils spiked with PCBs in concentrations as high as 500 ppm Aroclor 1242.

The extremely limited amount of data on field applications of biological processes to remediate PCB contaminated wastes makes it difficult to specify levels of detoxification possible in nonlaboratory conditions. Likewise, it is not possible to quantify chemical or matrix interferences which may be encountered, or the costs to be expected on a per unit basis. However, bioremediation is gaining favor in hazardous waste remediation in both Europe and the United States. As it is utilized, more data will be made available for assessing the efficiency of the technology for a myriad of contaminants, including PCBs. Specifically, the results of a field study of biodegradation in PCB contaminated Hudson River sediments, being conducted by General Electric, will make field application data available for future bioremediation schemes.

CHEMICAL DECHLORINATION

In 1978 at the Chemistry and Biosciences Laboratory, Franklin Research Center, a chemical reagent was synthesized and found to destroy PCBs by the process of dechlorination. Since that time, a family of alkali metal polyethylene glycolate (APEG) reagents have been developed which effectively dechlorinate PCBs in soils and liquids quickly. These reagents are known as KPEG or NaPEG, dependent on whether the alkali metal utilized is potassium or sodium. Research has shown that KPEG is more effective in destroying PCBs than NaPEG.

In a patented process, the KPEG reagent is prepared by reacting potassium hydroxide with one of several polyethylene glycols. This reaction produces an alkoxide which reacts with one of the chlorines on the aryl ring of the PCB to produce an ether (hydroxyl substituted aryl ring) and potassium chloride. The substitution of the chlorine atom with the ether-linked polyethylene glycol molecule detoxifies the PCB. Additional research indicated this process can also dechlorinate (and thereby detoxify) polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in either a solid or liquid matrix.

This process and variations of this process have undergone numerous laboratory studies and field demonstrations. A field demonstration conducted by EPA RREL in Guam on PCB contaminated soils utilized a batch reactor equipped with a mixer and an external steam jacket to allow for process heating. The steam jacket was designed to allow it to serve as a process cooling water system as well. A vent from the reactor to a condensate collection system was also provided. Following dechlorination the treated soil was allowed to cool. Sulfuric acid was then added to adjust the pH to the range of 6 to 9. Treated wastes with unacceptable concentrations of PCBs were subsequently re-treated to provide further dechlorination. Soil was discharged from the reactor, sampled and stored pending analytical results. Over several runs, approximately 15 cubic yards of soil with an average concentration of 3,500 ppm PCBs were treated to greater than 99% reduction of PCBs.

Waste soils pretreatment requirements (that is, largest particle size), are highly dependent on the physical configuration of the mixer employed. For the Guam demonstration, a maximum particle size of 1/2 inch was required to prevent fouling of the mixer blades against the reactor wall.

Implementation of this process utilizes commercially available process equipment, therefore is readily available. However, implementation of this process may be slowed by the need to obtain TSCA, RCRA, and potentially air and water

discharge permits. Additionally, care must be taken so as not to infringe on the patent holder's legal rights.

The cost to apply this technology will vary greatly depending upon the volume of treated waste and the current reagent prices. Cost estimates for treating soil in plants with a treatment capacity of 25 tons per batch operation have been estimated to range from \$242 to \$347 per ton of soil, with capital-related and chemical costs accounting for approximately 84 percent of total cost.

Several vendors offer dechlorination of PCB articles (transformers with PCB oil at concentrations greater than 500 ppm) and PCB contaminated equipment (transformers filled with dielectric fluid at concentrations between 50 and 500 ppm). The systems utilized are generally flatbed trailer mounted and operate using a closed loop circulation system. This allows for reclamation of transformer oil on-site, without draining it from the transformers. For a cost premium, the operation can be performed on energized transformers, reducing downtime. Proprietary reagents are utilized to dechlorinate, dewater, degassify and desludge transformer oils.

Properly utilized under the vendors' TSCA permit, these types of procedures allow for declassification of PCB and PCB contaminated electrical equipment. This in turn should reduce future liability for the electrical equipment owners, since equipment with less than 50 ppm PCBs is less likely to release harmful quantities of PCBs to the environment.

The specific nature of the proprietary reagents will determine any potential chemical and/or matrix interferences. Vendors need to be contacted for the costs of these operations. Factors which will affect the cost of treatment include type of unit to be serviced, the volume and concentration of dielectric fluid, access to equipment, and whether it will be energized or de-energized.

SOLVENT EXTRACTION

Solvent extraction of PCBs from soils makes use of PCBs' preferential solubility in oils and various extractants over water. HARBAUER, Sanivan Group, and Resources Conservation Company (RCC) have all developed processes when PCB contaminated oily soils or sludges mixed in an extraction vessel (generally a countercurrent soil washer or mixed reactor) with the appropriate solvent. During this step, the PCBs preferentially enter the oily solvent phase, leaving the soil phase with a greatly reduced PCB concentration. The solvent phase is decanted, and the soil phase is dried if necessary. The oily solvent fraction is then separated using standard separations techniques into oil, water, and solvent fractions. Ideally, solvent can be regenerated or recycled for future use, and all PCBs are concentrated within the oil fraction. These processes do not destroy PCBs, but rather, concentrate them into one phase of the original waste stream with a greatly reduced volume as compared to the original waste. The PCBs in the concentrated stream, generally the oil fraction, must then be either thermally or chemically destroyed as required by regulation.

HARBAUER and RCC have reported removal efficiencies on the order of 98 percent with oily soils contaminated with PCBs in the less than 20 ppm range during actual field scale on-site remediations. Sanivan Group will be conducting a field demonstration of their process under the auspices of EPA's SITE program on soils contaminated with PCBs in the range of 5 to 50 ppm.

Feed preparation requirements for solvent extraction processes are determined, in part, by the physical configuration of the extraction vessel. Maximum particle size and percent fines in the soil/waste matrix will likely be a factor for soil washing techniques, since a higher ratio of fines in the waste results in a greater volume of sludge requiring final disposition.

Potential chemical and matrix interferences will depend on the specific extractant and process equipment utilized. These

processes have been designed for treatment of contaminated soils, but modifications may be possible to allow for treatment of liquid phase wastes as well.

Soil treatment by solvent extraction is currently commercially available. Availability of the concentrated effluent must also be determined to judge overall implementability of these processes. As with all on-site treatment options it is recommended that the appropriate regulatory agency(s) be notified to expedite the approval/permitting process prior to implementation.

Costs are very site/waste specific. A potentially significant portion of the overall cost of treatment is the cost for destruction of the concentrated PCB waste stream. Vendors state that application of this technology is less expensive and more cost effective than incineration, but did not quote figures.

STABILIZATION

Chemical stabilization is a treatment process used to immobilize hazardous waste constituents in a solid matrix through mixing the original waste stream with additives and binders (that is, cement). For treating contaminated soil and sediments, the process generally involves excavation and subsequent conversion of the matrix to a solid mass which immobilizes leachable contaminants. An identical process can be applied to stabilize residual sludge streams with leachable contaminants resulting from various other treatment methods. Stabilized materials are typically sent to permitted landfills for disposal. Stabilization of soils may be applied in situ by adding stabilizing agents via a deep soil mixing auger, although effectiveness may vary. Stabilization reduces the mobility of contaminants, but does not destroy them. Therefore, the risk of exposure to humans or the environment resulting from leaching contaminants at low rates over the long term still exists.

As with all on-site treatment technologies, a determination of the permits required for remediation should be sought from the applicable regulatory agency(s).

Another limitation to stabilization of wastes is the inhibiting effect that organic constituents generally have on the curing process and final quality of the stabilized waste. Several vendors have developed proprietary additives which, when blended with cement, water and the contaminated soils, can overcome the deleterious effect of the organic constituents in the waste.

HAZCON, Inc. has performed a successful field demonstration of immobilizing low level (50 to 80 ppm) PCBs in soils in the presence of up to 25 percent by weight of oil and grease using a cement based process with their proprietary additive, Chloranan. Using a 10:10:1 ratio of waste:cement:Chloranan produced a solidified mass in which analysis of leachate could not detect PCBs at a detection limit of 1 ug/L. A volume increase of 120 percent was observed, and cost of \$250 per ton for the demonstration was calculated.

International Waste Technologies (IWT) has developed their own proprietary soil stabilization additive, HWT-20. IWT has performed a demonstration of in-situ stabilization of soils contaminated with PCBs in concentrations up to 950 ppm (with most of the samples under 300 ppm) utilizing HWT-20 and a deep soil mixing technique developed by Geo-Con, Inc. Results of this demonstration, conducted as part of EPA RREL's SITE program, indicate that the process may immobilize PCBs. However, due to the low concentrations of PCBs in the treated soils (after dilution resulting from addition of cement and HWT-20), absolute confirmation of this tentative finding could not be proven. Additionally, due to the very limited amount of volatile organics detected in the waste matrix, it is unable to predict if HWT-20 can counteract their effect on the final product. Furthermore, while unconfirmed compressive strength, permeability and wet/dry weathering tests indicated the solidified mass could maintain its integrity over a long period of time, unsatisfactory water loss was observed during

the freeze/thaw weathering tests. As compared to HAZCON's process, volume increase (8.5 percent) and cost (\$194 per ton) observed in the IWT/Geo-Con process were moderate. However, due to uncertainties in the quality of the final product, further studies should be conducted prior to commercial application of this process.

CONCLUSIONS

When selecting a technology to treat PCB contaminated wastes, it is necessary to take into account the applicability of the technology to the specific waste stream. Availability and reliability of the technology is also of vital importance. As delineated in this paper, there are currently several technologies (for example, incineration, chemical dechlorination and waste water treatment technologies) which have proven their ability to destroy PCBs and for which a significant amount of applications data exists. There are several others which can be considered emerging technologies—they have been proven technically viable, yet limited field applications data reduces the ability to effectively judge the feasibility of utilizing these technologies to treat specific waste streams. These emerging technologies include in-situ vitrification, solvent extraction, surface decontamination, and stabilization. Finally, biodegradation and destruction using quicklime are developmental technologies. A significant amount of study will be required to determine if these technologies will prove effective in destruction of PCBs.

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Granular Activated Carbon Pilot Treatment Studies for Explosives Removal From Contaminated Groundwater

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Manufacturing activities at Army Ammunition Plants (AAPs) result in the production of organic wastewaters that contain both explosive residues and other organic chemicals. As a result of past waste practices at such plants, explosive residues may leach through the soil and contaminate groundwater. Two pilot studies were performed to evaluate the use of granular activated carbon (GAC) to treat groundwater contaminated with explosives at Badger AAP and Milan AAP. An additional goal of the Badger AAP study was to examine the potential discharge of explosives 2,4-DNT and 2,6-DNT from a packed column air stripper used to remove volatile organic compounds from groundwater. A laboratory method was developed for the BAAP study to permit lower detection levels for 2,4-DNT and 2,6-DNT (0.46 $\mu\text{g}/\text{L}$ and 0.017 $\mu\text{g}/\text{L}$, respectively). The studies concluded that removal of explosives from groundwater using continuous flow GAC is feasible.

INTRODUCTION

The United States Army operates explosives plants that load, assemble, and pack (LAP) explosives into military ordnance. Activities at such plants produce process wastewaters that contain both explosives residues and other organic chemicals. Several treatment technologies have been developed and are currently in use to treat these wastewaters for final discharge.

Past waste handling practices at explosives LAP plants often utilized unlined lagoons or pits to contain process wastewaters. As a result of this practice, some explosives residues have leached through the soil to contaminate groundwater. Therefore, groundwater treatment may be required. Based upon process wastewater treatment experience, potentially applicable treatment technologies are available. However, the similarities and differences between process wastewaters and explosives-contaminated groundwater should be considered before transferring technologies from one application to another.

Process wastewaters at explosives LAP plants are often treated by activated carbon adsorption. This treatment has been documented in the literature [1, 2, 3, 4]. Therefore, based

upon process wastewater treatment experience, activated carbon adsorption would likely work for the treatment of explosives-contaminated groundwater. However, because of the similarities and differences between process wastewaters and explosives-contaminated groundwater, the feasibility of using activated carbon adsorption for treatment of groundwater should be determined.

Hinshaw et al. [5] present a multiphase study providing quantitative data on the ability of activated carbon to remove the nitroaromatics 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), cyclotrimethylenetrinitramine (RDX), and cyclotetramethylenetetranitramine (HMX) from pink water. The study included preliminary activated carbon screening, isotherm tests of activated carbon, preliminary column tests of selected activated carbons, four-in-series column tests, and an economic analysis of activated carbon. Isotherm tests on five different carbons were conducted to select the best performing carbon for further testing using continuous-flow columns. Pilot-scale column tests were subsequently performed with four columns in-series using one of the five carbons for the treatment of actual ammunition plant pink water. Effluent criteria (40 $\mu\text{g}/\text{L}$ TNT, 30 $\mu\text{g}/\text{L}$ RDX, 30 $\mu\text{g}/\text{L}$ HMX, and 0.7 $\mu\text{g}/\text{L}$

2,4-DNT) were generally met for RDX, HMX, and 2,4-DNT, but not for TNT. The TNT performance limitation was determined to be a physicochemical phenomenon. This phenomenon did not appear during the isotherm tests and points to the importance of performing actual column tests with the wastewaters to be treated.

Groundwater in the area of the Propellant Burning Grounds at Badger Army Ammunition Plant (BAAP) in Baraboo, Wisconsin, has been found to be contaminated with explosives compounds, including dinitrotoluene isomers, volatile organic compounds (VOCs), and related degradation products [6]. A barrier well network to intercept the advancing contaminant plume with associated treatment using air stripping and/or granular activated carbon (GAC) has been proposed.

Explosives-contaminated water has percolated from the O-line ponds at the Milan Army Ammunition Plant (MAAP) in Milan, Tennessee, into the upper and middle part of the Clairborne aquifer underlying the facility. Migration of these wastes is expected to continue in the groundwater flow system and thereby contaminate additional groundwater and possibly surface water in the area. The chemical wastes that are of major concern at MAAP are 2,4,6-trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), 2,4,6-trinitrophenylmethylnitramine (Tetryl), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 1,3-dinitrobenzene (1,3-DNB), 1,3,5-trinitrobenzene (1,3,5-TNB), and nitro-benzene (NB).

The primary objective of these pilot studies was to determine the feasibility of using GAC to treat explosives-contaminated groundwater. The explosive contaminants studied were TNT, RDX, HMX, Tetryl, 2,4-DNT, 2,6-DNT, 1,3-DNB, 1,3,5-TNB, and NB. The studies included preliminary batch (isotherm) testing followed by column testing using a continuous-flow pilot plant. Since groundwater contamination at BAAP includes VOCs, an air stripper was used in conjunction with GAC treatment. The secondary objective of the pilot study at BAAP was to examine the potential for discharge of explosive components from the air stripper.

ISOTHERM TEST PROGRAM

Laboratory GAC isotherm studies were conducted to evaluate the ability of activated carbon to remove 2,4-DNT and 2,6-DNT from groundwater at BAAP and TNT, RDX, HMX, Tetryl, 2,4-DNT, 2,6-DNT, 1,3,5-TNB, and NB from the explosives-contaminated groundwater at MAAP. Five different types of granular activated carbon were evaluated in both studies in terms of: (1) relative adsorbability of explosives; (2) adsorption capacities and associated exhaustion rates for explosives; (3) degrees of removal based on desired effluent objectives; and (4) preferential adsorption of component groups. The isotherm studies also evaluated the effect of an acidic pH (4.0) on adsorption capacities.

Isotherm testing consisted of a series of batch adsorption experiments in which multiple aliquots of groundwater from BAAP and MAAP were treated with varying dosages of GAC. The test containers were agitated to achieve equilibrium between the liquid phase and the solid phase. The GAC was then filtered out of the solution and the filtrate was analyzed to determine the equilibrium concentration of the parameters (or adsorbate) of interest. The data obtained from the analysis were interpreted by plotting the amount of adsorbate adsorbed per unit weight of activated carbon versus the equilibrium concentration of adsorbate remaining in solution.

Groundwater samples from BAAP received additional treatment prior to isotherm testing. They were aerated for 1 hour and 15 minutes (to simulate air stripping) to strip off volatiles present in the groundwater. The pHs of the groundwater samples before aeration were in the range of 7.0 to 7.5. After aeration, the pH of the groundwater samples had increased to range from 8.3 to 8.7. Sulfuric acid (H₂SO₄) was added to the

aerated groundwater samples to lower the pH to required levels prior to contacting the groundwater with carbon.

ISOTHERM TEST RESULTS

The Freundlich adsorption equation was used in presenting the carbon isotherm test results. Isotherms were developed for BAAP for 2,4-DNT and 2,6-DNT by plotting the adsorption data on logarithmic coordinates as carbon loading (q_e) versus the equilibrium concentration (C_e) of compound remaining in the groundwater sample. The empirical constants of the Freundlich equation for the five test carbon isotherms are presented in Table 1.

On the basis of adsorption capacities for 2,4-DNT and 2,6-DNT, Filtrasorb 300 and Hydrodarco 4000 were judged to be the best performing GACs for removing both contaminants from groundwater at BAAP. The maximum saturation capacities (theoretical maximum loading) for Filtrasorb 300 and Hydrodarco 4000 were estimated by extrapolating the isotherms to $(q_e)C_0$. The carbon loading thus obtained corresponds by definition to a condition when all the carbon is in equilibrium with the influent concentration (C_0). In a carbon column treatment system, this equates to operating a GAC system until the concentration of a particular compound at the column effluent equals the influent concentration. The equilibrium q_e values at different influent concentrations of 2,4-DNT and 2,6-DNT for the five GACs are presented in Table 2.

Therefore, as a result of this isotherm testing program, Filtrasorb 300 and Hydrodarco 4000 were selected for further testing, using continuous-flow GAC columns at BAAP.

The empirical constants of the Freundlich adsorption equation for the five test carbon isotherms for MAAP are presented in Table 3 for TNT and RDX. These constants for the three Filtrasorb carbons could not be determined for TNT because it was present at concentrations below its detection limit in all of the filtrates. For this same reason, the empirical constants of the Freundlich adsorption equation for all five carbons for the other seven explosives could not be determined.

The maximum saturation capacities (theoretical maximum loading) for all five carbons for RDX were estimated by ex-

Table 1 Empirical Constants of Freundlich Adsorption Equation^a for Five GACs Using Groundwater from Monitoring Well PBN82-02C at the Badger Army Ammunition Plant

Activated Carbon Type	2,4-DNT Isotherms		2,6-DNT Isotherms	
	K^b	$1/n^c$ (slope)	K^b	$1/n^c$ (slope)
Filtrasorb 200	0.085	0.077	0.03	0.022
Filtrasorb 300	0.075	0.067	0.09	0.086
Filtrasorb 400	(0.9) ^d	(2.72)	0.09	0.086
Hydrodarco 3000	0.02	0.014	0.03	0.029
Hydrodarco 4000	0.2	0.263	0.035	0.024

^a $q_e = X/M = KC_e^{1/n}$.

where,

q_e = Carbon loading, mg compound/mg carbon, dimensionless.

$X = C_0 - C_e$, the amount of compound adsorbed for a given volume of solution, mg/L.

M = Carbon dosage, mg/L.

C_0 = Initial concentration of compound, mg/L.

C_e = Concentration of compound remaining in solution, mg/L.

K = Freundlich constant (mg/L)^{-1/n}.

n = Empirical constant, dimensionless

^bIntercept at $C_e = 1.0$ mg/L on the isotherm line. This intercept was determined by extrapolation.

^cSlope of the line within the concentration range of 0.01-1.0 mg/L.

^dBy extrapolation from the maximum equilibrium concentration of 0.06 mg/L (obtained at the lowest carbon dosage of 10 mg/L) to a concentration of 1.0 mg/L.

Table 2 Maximum Saturation Capacities (q_s) for Five GACs Tested for at the Badger Army Ammunition Plant

Carbon Type	Nitrobody	Influent Concentration (mg/L) ^a	Saturation C_0 Capacity (q_s) (mg/mg)
Filtrisorb 300	2,4-DNT	2	0.1
		10	0.21
	2,6-DNT	1	0.09
		4	0.21
Hydrodarco 4000	2,4-DNT	2	0.28
		10	0.62
	2,6-DNT	1	0.03
		4	0.07
Filtrisorb 200	2,4-DNT	2	0.10
		10	0.22
	2,6-DNT	1	0.03
		4	0.06
Filtrisorb 400	2,4-DNT	2	— ^b
		10	— ^b
	2,6-DNT	1	0.09
		4	0.21
Hydrodarco 3000	2,4-DNT	2	0.02
		10	0.03
	2,6-DNT	1	0.03
		4	0.12

^aInfluent concentrations correspond to those anticipated from previous work (10 mg/L for 2,4-DNT and 4 mg/L for 2,6-DNT) and to those actually found in the groundwater sample used for isotherm tests reported here (2 mg/L for 2,4-DNT and 1 mg/L for 2,6-DNT).

^bDue to an elevated detection limit caused by sample interference, the exact value for the data point corresponding to this carbon dosage could not be determined.

trapolating their isotherms to C_0 . This gives a q_s that corresponds to a condition in which all the carbon is in equilibrium with the initial concentration of RDX. In a continuous-flow GAC column, this condition occurs when the RDX concentration in the effluent is the same as that in the influent. However, this does not occur in practice, because normally

Table 3 Empirical Constants for Freundlich Adsorption Equation^a for Five Test Carbons Using Groundwater from Monitoring Well M1051 at the Milan Army Ammunition Plant

Activated Carbon Type	TNT		RDX	
	Isotherms K^b	$1/n^c$	Isotherms K^b	$1/n^c$
Filtrisorb 200	ND ^d	ND ^d	0.052	0.535
Filtrisorb 300	ND ^d	ND ^d	0.031	0.413
Filtrisorb 400	ND ^d	ND ^d	0.049	0.555
Hydrodarco 4000	0.128	0.828	0.0012	0.100
Atochem, Inc. GAC 830	0.136	0.642	0.045	0.630

^a $q_s = X/M = KC_e^n$, where,

- q_s = Carbon loading, mg compound/mg carbon, dimensionless.
- $X = C_0 - C_e$, the amount of compound adsorbed for a given volume of solution, mg/L.
- M = Carbon dosage, mg/L.
- C_0 = Initial concentration of compound, mg/L.
- C_e = Concentration of compound remaining in solution, mg/L.
- K = Freundlich constant (mg/L)^{-1/n}.
- n = Empirical constant, dimensionless

^bIntercept at $C_e = 1.0$ mg/L on the isotherm line. This intercept was determined by extrapolation.

^cSlope of the line within the concentration range of 0.01–1.0 mg/L.

^dND = Not determinable.

the column service is terminated when the effluent concentration reaches a predetermined effluent limit. In addition, maximum saturation capacities for Hydrodarco 4000 and Atochem, Inc. GAC 830 for TNT were estimated by extrapolating their isotherms to C_0 .

Because of inconclusive results on the effect of pH on the activated carbon adsorption of the groundwater from monitoring well M1051 at MAAP, the continuous-flow GAC columns at MAAP were run at pH 7.0. This decision was supported by the results on the effect of pH described in the previous pilot study at Badger Army Ammunition Plant (BAAP) [7]. In that study, the results of the isotherm tests for Filtrisorb 400, using explosives-contaminated groundwater from monitoring well PBN82-02C at BAAP, showed that relatively higher adsorption capacities were obtained at neutral pH (7.0) than at acidic pH (4.0). Even though previous results in the literature [3] showed the opposite to be true for TNT and other nitroaromatics, greater weight was given to the BAAP report because it represented the most recent experience with explosives-contaminated groundwater.

PILOT STUDIES

Activated Carbon Pilot-Scale Test at BAAP

The continuous-flow column testing was conducted at BAAP using the two types of carbons selected from the batch (isotherm) testing. A schematic of the pilot plant, including the air stripper, is shown in Figure 1. Two continuous-flow column tests were performed, each using two carbon columns.

For each test, the total groundwater flow was split between the two test trains (A and B) at different proportions depending on the desired hydraulic loading rates. The two columns in Train A and Train B contained carbon types designated as A and B, respectively.

All of the tests were conducted inside the test building located at BAAP. The test area was maintained at a minimum temperature of 50°F. The hydraulic surface loading rates that were employed during the pilot tests were 3, 5, and 7 gpm/ft². These values are within the range of hydraulic surface loading rates that are normally used in full-scale operation of GAC systems.

Adsorption and breakthrough characteristics were studied in the first column of each parallel pair. The function of the second column was to maintain effluent (discharge) quality within acceptable limits while allowing contaminant leakage up to influent levels (total exhaustion of capacity) of the first column. Influent and effluent (first column as well as second column) were monitored for pH and temperature at regular time intervals.

An air stripper was used to remove volatile solvents from the groundwater prior to its entering the GAC pilot plant. The primary function of the air stripper in this project was to minimize any effects of these solvents on the evaluation of activated carbon adsorption of explosives. The potential for discharge of explosives into the air stream was examined by emissions testing of the exhaust stack. Sampling points were located approximately 6 feet above (downstream from) the

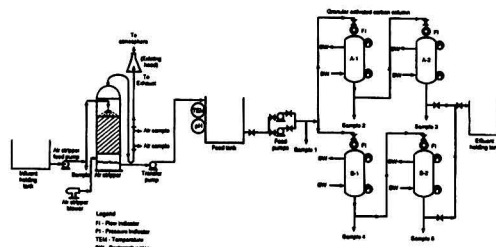


FIGURE 1. BAAP Pilot Treatment Plant Configuration

Table 4 Summary of Granular Activated Carbon (GAC) Columns Operating and Performance Data for Pilot Tests at the Milan Army Ammunition Plant

	Test One		Test Two		Test Three	
	Starting Date: 7 September 1989 Ending Date: 15 September 1989 Column Inner Diameter: 4.25 in. 0.354 ft) Column Area: 0.0985 ft ² Bed Volume: 0.394 ft ³ (2.94 gal.)	Column A1	Starting Date: 19 September 1989 Ending Date: 6 October 1989 Column Inner Diameter: 4.25 in. 0.354 ft) Column Area: 0.0985 ft ² Bed Volume: 0.394 ft ³ (2.94 gal.)	Column A1	Starting Date: 16 October 1989 Ending Date: 15 December 1989 Column Inner Diameter: 4.25 in. 0.354 ft) Column Area: 0.0985 ft ² Bed Volume: 0.197 ft ³ (1.47 gal.)	Column B1
GAC Used	Atochem, Inc. GAC 830	Atochem, Inc. GAC 830	Atochem, Inc. GAC 830	Calgon Filtrisorb 300	Atochem, Inc. GAC 830	Calgon Filtrisorb 300
Flow Rate	1.0 gpm	0.2 gpm	0.7 gpm	0.7 gpm	0.75 gpm	0.75 gpm
Hydraulic Loading	10.15 gpm/ft ²	2.03 gpm/ft ²	7.11 gpm/ft ²	7.11 gpm/ft ²	7.6 gpm/ft ²	7.6 gpm/ft ²
Bed Depth	4 ft	4 ft	4 ft	4 ft	2 ft	2 ft
Empty-Bed Contact Time	3.0 min.	14.7 min.	4.2 min.	4.2 min.	2.0 min.	2.0 min.
Final Effluent Levels (µg/L)						
TNT (Influent 433 µg/L)	ND	ND	ND	ND	88.6 µg/L	192 µg/L
RDX (Influent 487 µg/L)	7.05 µg/L	ND	ND	ND	315 µg/L	344 µg/L
HMX (Influent 3.4 µg/L)	ND	ND	ND	ND	ND	ND
Tetryl (Influent ND)	ND	ND	ND	ND	ND	ND
2,4-DNT (Influent 10.8 µg/L)	ND	ND	ND	ND	3.6 µg/L	ND
2,6-DNT (Influent ND)	ND	ND	ND	ND	ND	ND
1,3-DNB (Influent 3.2 µg/L)	ND	ND	ND	ND	9.91 µg/L	14.9 µg/L
1,3,5-TNB (Influent 21.4 µg/L)	ND	ND	ND	ND	ND	ND
NB (Influent ND)	ND	ND	ND	ND	ND	ND
Run Time	7.6 days	7.6 days	16.5 days	16.5 days	54.5 days	54.5 days

Notes: ND = Not detected.
Concentrations in parentheses are average influent concentrations.

expansion point in order to eliminate any effects of flow disturbances caused by the expansion. Samples from the exhaust stack were analyzed for explosives components (2,4-DNT and 2,6-DNT). The adequacy with which the air stripper removed volatiles was verified by comparing GAC pilot-plant influent levels to those in the untreated groundwater.

Samples for explosives analysis were collected from the air stripper exhaust duct using an EPA Modified Method 5 (MM5) sampling train. The train was further modified by the inclusion of an additional XAD-2 resin trap (a total of two) to ensure complete collection of target explosives. Sampling was conducted along the horizontal axis of the 8-inch inner diameter duct. The number of sample points and the sampling duration were determined on-site, with a 4-hour sample time used at four traverse points. Sampling was isokinetic (90 to 110%). Volumetric flow rate was determined by EPA Methods 1 and 2 as part of the MM5 train. Moisture content was determined using the EPA MM5 sample train used for collection of explosives. Triplicate test repetitions were performed for each emission parameter.

A mobile field laboratory was used to provide rapid turnaround of the large number of samples generated during pilot testing. Samples were analyzed in the field laboratory for dinitrotoluenes by liquid/liquid extraction and electron capture gas chromatography (GC), utilizing USATHAMA Method UW01. The following modifications to Method UW01 were made for field use:

1. Use injection volume of 5 mL.
2. Calibration curves of 1x, 5x, 10x, 50x, and 100x.
3. Daily QC of blank and 10x spike.
4. Final 10x calibration standard.

Detection limits were determined by instrument sensitivity.

In order to verify treatability at very low contaminant influent and effluent concentrations, WESTON's Analytics Division obtained certification from USATHAMA for a low-level DNT analytical method employing liquid/liquid extraction and electron capture detector QC analysis. The detection limits established in this certification effort were 0.46 µg/L for 2,4-DNT and 0.017 µg/L for 2,6-DNT. Following certification, this method was used for explosives analyses at the WESTON Analytics Division laboratory. The WESTON Analytics Division laboratory data were used to verify the field data.

Samples were analyzed by U.S. EPA Method 8010 for carbon tetrachloride, chloroform, trichloroethylene, and 1,1,1-trichloroethane. Detection levels of 1 ppb were obtained with Method 8010.

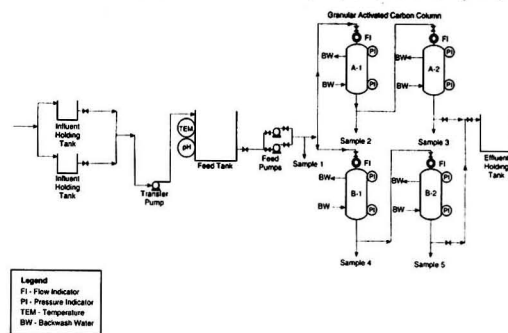


FIGURE 2. MAAP GAC Pilot Plant Configuration

was decided by WESTON and USATHAMA that breakthrough would not be reached in a reasonable amount of time for study purposes using the operating parameters in Table 4. None of the contaminants of concern in this table were detected in the effluent samples during Test Two.

Test Three was run for a total of 54.5 days, at which time, because of cold weather, it was decided by WESTON and USATHAMA that the unit should be shut down so that no damage would occur to the system. Of the contaminants of concern in Table 4, only TNT, RDX, 2,4-DNT, and 1,3,5-TNB were detected in the effluent samples during Test Three.

The analytical parameters for all tests were TNT, RDX, HMX, Tetryl, 2,4-DNT, 2,6-DNT, 1,3-DNB, 1,3,5-TNB, and NB. A total of 750 samples was analyzed by high-performance liquid chromatography (HPLC) for these parameters at the field laboratory at MAAP, utilizing USATHAMA Method UW01, Explosives in Waters. The samples included influent samples to the GAC unit and effluent samples from columns A1, A2, B1, and B2. The field laboratory was critical in providing rapid turnaround, facilitating operating decisions, and protecting effluent quality. In addition, 42 samples were sent to WESTON's Analytics Division for similar analysis. These samples represented 6% of the field laboratory samples analyzed and verified field laboratory performance.

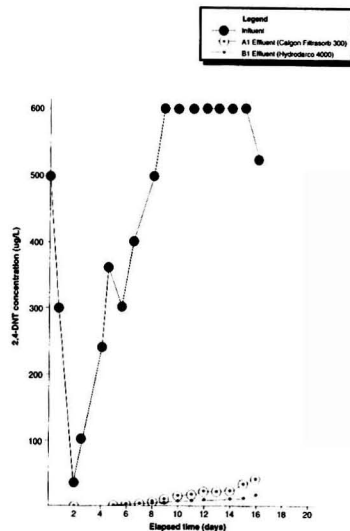


FIGURE 3. 2,4-DNT Concentration Using Early Morning Data (0600-0800) from Field Laboratory Results for Run One (Starting 15 February 1989) at BAAP

Activated Carbon Pilot-Scale Test at MAAP

The continuous-flow column testing at MAAP was conducted using the two types of carbon selected from the batch (isotherm) testing. A schematic of the pilot plant is shown in Figure 2. The air stripper was not used at MAAP because volatiles were not detected in the groundwater used for the pilot test. During the field test program at MAAP, three continuous-flow column tests were performed, each using two carbon column trains. The operating and performance data for Tests One, Two, and Three are presented in Table 4.

Test One was run for a total of 7.6 days, at which time it was decided by WESTON and USATHAMA that breakthrough would not be reached in a reasonable amount of time for study purposes using the operating parameters in Table 4. Except for RDX, none of the contaminants of concern in this table were detected in the effluent samples during Test One. RDX was detected in column A1's effluent sample, but at a concentration that was approximately 1% of its influent concentration.

Test Two was run for a total of 16.5 days, at which time it

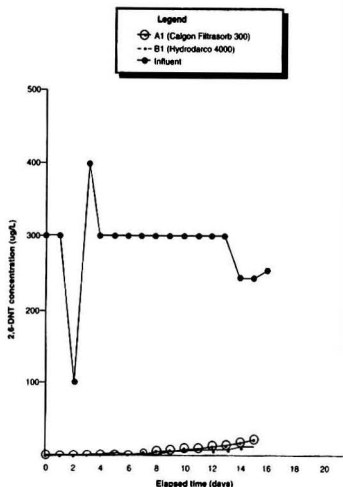


FIGURE 4. 2,6-DNT Concentration Using Early Morning Data (0600-0800) from Field Laboratory Results for Run One (Starting 15 February 1989) at BAAP

DISCUSSION OF RESULTS

At the influent concentrations of groundwater from monitoring well PBN-82-02C at BAAP, influent surface loading rates of 3.0 to 7.0 gpm/ft² and an influent hydraulic loading rate of 1.5 to 3.5 gpm/ft³, GAC columns employing either Filtrasorb 300 or Hydrodarco 4000 can provide run lengths of at least 16,130 gallons (10,970 bed volumes) while providing 2,4-DNT and 2,6-DNT removals of greater than 90%. Under conditions employed in this study, explosives concentrations could be reduced below detection limits (in this study, approximately 0.46 µg/L for 2,4-DNT and 0.017 µg/L for 2,6-DNT) for approximately 4,120 gallons (2,800 bed volumes) at the highest loading rate for 2,4-DNT and for approximately 180 gallons (123 bed volumes) at an intermediate loading rate for 2,6-DNT. Figures 3 through 6 summarize experimental results.

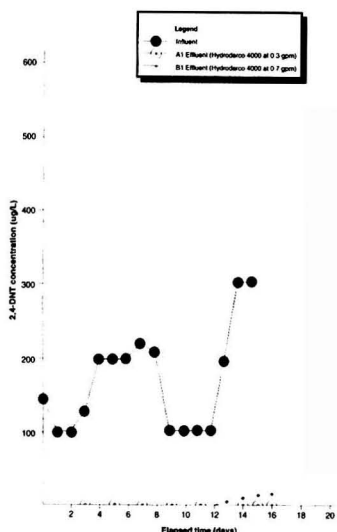


FIGURE 5. 2,4-DNT Concentration Using Early Morning Data (0600-0800) from Field Laboratory Results for Run Two (Starting 8 March 1989) at BAAP

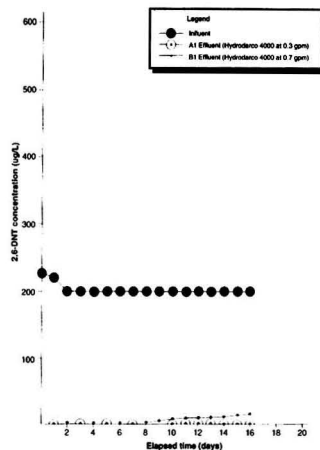


FIGURE 6. 2,6-DNT Concentration Using Early Morning Data (0600-0800) from Field Laboratory Results for Run Two (Starting 8 March 1989) at BAAP

Table 5 shows that generally good agreement was obtained between the mobile (field) laboratory analyses and those performed by WESTON's Analytics Division, particularly considering the difference in detection limits between the analytical methods.

Tables 6 and 7 summarize operating characteristics for runs one and two. Based upon the flow rate, observed (average) influent concentrations, and total operating time, the total mass loading of each explosive to each column was calculated. Based upon the total amount of carbon in each column and the specific adsorption capacity of the carbon for the explosive (as determined from the isotherm tests), the total column capacity for each explosive was calculated. Finally, from the mass of explosive applied and the capacity of the column, the percent utilization of column capacity was calculated. As noted previously, the effluent (that is, not adsorbed) fraction of the explosives did not exceed 10%, and most of the time was substantially lower. Therefore, for this calculation the difference between the total mass of explosive applied and that adsorbed (as would be estimated by integration under the respective concentration curves in Figures 3 through 6) was considered minor.

Table 6 shows that after 16 days of operation at the indicated loading, a relatively small fraction of each carbon's capacity for each explosive was utilized. Table 7 suggests the same conclusions for all three loading rates using Hydrodarco 4000. It should be noted that, even though the maximum hydraulic loading in run two was higher than in run one, the explosives concentrations in the groundwater had fallen as compared to run one, resulting in a lower mass loading rate of explosives to the column. Longer activated carbon column contact times (which in this study did not exceed 5 minutes) may provide even longer column lives for a given influent concentration.

These data clearly show that the use of new granular activated carbon in continuous-flow columns produced very low effluent explosives concentrations, generally in the low parts-per-billion (ppb) range during the early portions of each run. In most test runs effluent explosives levels rose gradually through the duration of the experiment. However, in no run did the effluent concentration of either 2,4-DNT, or 2,6-DNT exceed 10% of the respective (average) influent concentration before it became necessary to terminate the run. In the first run, which examined both selected carbons at an identical influent rate of 0.5 gpm, effluent levels of 2,4-DNT reached 40 µg/L (Filtrasorb 300) and 14 µg/L (Hydrodarco 4000) at the end of 16 days of operation (11,520 gallons—7,835 bed

Table 5 WESTON's Analytics Division Results Versus WESTON Field Laboratory Results for Run Two at the Badger Army Ammunition Plant

Sample ID	Hours into Test	WESTON Analytics Laboratory Results Concentration ($\mu\text{g/L}$)		Field Laboratory Results Concentration ($\mu\text{g/L}$)	
		2,4-DNT	2,6-DNT	2,4-DNT ^a	2,6-DNT
Column A1 (Hydrodarco 4000 at 0.3 gpm)					
8 March 1989, 16:00	2	18.10	9.80	0.7 ^b	0.6 ^b
9 March 1989, 16:00	26	<0.46	0.30	0.4	0.4
10 March 1989, 16:00	50	<0.46	0.27	—	—
11 March 1989, 16:00	74	<0.46	0.26	0.3	0.3
12 March 1989, 16:00	98	<0.46	0.20	0.25	0.25
Column B1 (Hydrodarco 4000 at 0.7 gpm)					
8 March 1989, 16:00	2	0.50	0.19	0.2 ^b	0.2 ^b
9 March 1989, 4:00	14	<0.46	0.14	ND ^c	0.1 ^c
9 March 1989, 16:00	26	<0.46	0.08	ND	0.1
10 March 1989, 4:00	38	<0.46	0.07	ND ^c	0.1 ^c
10 March 1989, 16:00	50	<0.46	0.06	—	—
11 March 1989, 4:00	62	<0.46	0.05	ND ^d	0.1 ^d
11 March 1989, 16:00	74	<0.46	0.05	ND	0.1
12 March 1989, 4:00	86	<0.46	0.05	ND ^d	0.1 ^d
12 March 1989, 16:00	98	<0.46	0.04		

^aND = Below detection limit.

^bSample taken at 14:00 hours on 8 March 1989.

^cSamples taken at 6:00 hours.

^dSamples taken at 8:00 hours.

volumes). Effluent levels for 2,6-DNT at this point were 24 $\mu\text{g/L}$ (Filtrisorb 300) and 15 $\mu\text{g/L}$ (Hydrodarco 4000).

The second run employed a higher flow rate through one carbon train (0.7 gpm). Since the output of the monitoring well was limited to approximately 1.0 gpm, the other column train operated at 0.3 gpm. In this run, both column trains employed Hydrodarco 4000 carbon, which had provided the lower final effluent concentrations for both contaminants in run one. After a throughput volume of 16,130 gallons (10,970 bed volumes) for the higher (0.7 gpm) flow rate train, effluent 2,4-DNT was 10 $\mu\text{g/L}$ and effluent 2,6-DNT was 1.6 $\mu\text{g/L}$. Effluent levels were 0.48 $\mu\text{g/L}$ for 2,4-DNT and 0.12 $\mu\text{g/L}$ for

2,6-DNT for the lower (0.3 gpm) flow rate train. As with run one, complete breakthrough was not observed, and with the concurrence of USATHAMA, run two was terminated at this point.

It should be noted that a major contributing factor to the inability to obtain breakthrough within available time periods was the low influent concentration of the contaminants of concern, at approximately two orders of magnitude lower than anticipated. The average influent 2,4-DNT concentration for the second run was 50% lower than the first run. Similarly, the average influent 2,6-DNT concentration for the second run was 33% lower than the first run.

Table 6 Activated Carbon Column Operating and Performance Data for Run One at the Badger Army Ammunition Plant Hydrodarco 4000 Versus Calgon Filtrisorb 300

Column Outer Diameter	= 5 inches (0.42 ft)	
Column Inner Diameter	= 4.25 inches (0.354 ft)	
Column Area	= 0.0985 ft ²	
Bed Volume (at 2-ft depth)	= 0.197 ft ³ (1.47 gallons)	
	Hydrodarco 4000	Filtrisorb 300
Flow Rate	0.5 gpm	0.5 gpm
Surface Loading Rate	5.0 gpm/ft ²	5.0 gpm/ft ²
Contact Time	3.0 min.	3.0 min.
Hydraulic Loading	2.50 gpm/ft ³	2.50 gpm/ft ³
2,4-DNT Influent Concentration (avg.)	0.42 mg/L	0.42 mg/L
2,6-DNT Influent Concentration (avg.)	0.3 mg/L	0.3 mg/L
2,4-DNT Capacity (rate)*	0.12 lb/lb	0.05 lb/lb
2,6-DNT Capacity (rate)*	0.016 lb/lb	0.044 lb/lb
Weight of Carbon in Column	4.8 lb	5.8 lb
Column 2,4-DNT Capacity (wt)	0.576 lb	0.290 lb
Column 2,6-DNT Capacity (wt)	0.077 lb	0.255 lb
Total 2,4-DNT Loading to Column (lb)	0.045	0.045
Total 2,6-DNT Loading to Column (lb)	0.029	0.029
2,4-DNT Capacity Utilized	7.8%	15.5%
2,6-DNT Capacity Utilized	37.7%	11.4%
Run Time (days)	16	16

*From isotherm data.

Table 7 Activated Carbon Column Operating and Performance Data for Hydrodarco 4000 from Runs One and Two at the Badger Army Ammunition Plant

	Column Outer Diameter	= 5 inches (0.42 ft)		
	Column Inner Diameter	= 4.25 inches (0.354 ft)		
	Column Area	= 0.0985 ft ²		
	Bed Volume (at 2-ft depth)	= 0.197 ft ³ (1.47 gallons)		
	Flow Rate	0.3 gpm (Run Two)	0.5 gpm (Run One)	0.7 gpm (Run Two)
	Surface Loading Rate	3.0 gpm/ft ²	5.0 gpm/ft ²	7.0 gpm/ft ²
	Contact Time	5.0 min.	3.0 min.	2.2 min.
	Hydraulic Loading	1.50 gpm/ft ³	2.50 gpm/ft ³	3.50 gpm/ft ³
	2,4-DNT Influent Concentration (avg.)	0.17 mg/L	0.42 mg/L	0.17 mg/L
	2,6-DNT Influent Concentration (avg.)	0.2 mg/L	0.3 mg/L	0.2 mg/L
	2,4-DNT Capacity (rate)*	0.06 lb/lb	0.12 lb/lb	0.06 lb/lb
	2,6-DNT Capacity (rate)*	0.013 lb/lb	0.016 lb/lb	0.013 lb/lb
	Weight of Carbon in Column	4.8 lb	4.8 lb	4.8 lb
	Column 2,4-DNT Capacity (wt)	0.288 lb	0.576 lb	0.288 lb
	Column 2,6-DNT Capacity (wt)	0.062 lb	0.077 lb	0.062 lb
	Total 2,4-DNT Loading to Column (lb)	0.0098	0.045	0.023
	Total 2,6-DNT Loading to Column (lb)	0.012	0.029	0.027
	2,4-DNT Capacity Utilized (lb)	3.4%	7.4%	8.0%
	2,6-DNT Capacity Utilized	19.4%	37.7%	43.5%
	Run Time (days)	16	16	16

*From isotherm data.

The explosives emissions evaluation during this study consisted of three separate tests during which exhaust gases from the stripper were sampled and analyzed. All three air stripper tests were conducted during the second GAC test run. Stack gases were near saturation at approximately 72% relative humidity for all three runs. Explosives emission data from all three test runs are presented in Table 8.

Table 8 indicates that explosives were detected in the exhaust of the stripper. The feed rate to the stripper was approximately 4 gpm of explosives-contaminated water for each time period for each test; therefore, over a 4-hour period approximately 960 gallons of water were processed through the stripper. The contaminated groundwater influent contained 0.18 mg/L of both 2,4-DNT and 2,6-DNT for emissions tests one and two, and 0.34 mg/L of 2,4-DNT and 0.19 mg/L of 2,6-DNT for test three. These concentrations equate to 3.62×10^{-4} lb/hr for 2,4-DNT and 2,6-DNT for tests one and two, 6.84×10^{-4} lb/hr for 2,4-DNT test three, and 3.82×10^{-4} lb/hr for 2,6-

DNT test three. When comparing input concentrations to output air emissions, on the average 99.8% of 2,4-DNT and 99.5% of 2,6-DNT remained in the liquid phase and did not exit through the stripper air exhaust.

It was found that the "U" connector at the base of the stack did accumulate contaminated condensate through the course of each test. This water was analyzed and found to contain almost identical levels of explosives as the feed water. Therefore, it can be assumed that this condensate is a result of mist carryover through the air stripper mist eliminator and that this water should be returned to the feed tank for reprocessing.

Samples from the GAC influent tank indicated that the GAC influent contained very low concentrations of volatiles, as compared to the raw groundwater. Therefore, the air stripper was effective for its intended purpose of removing volatiles and minimizing their potential impact on the GAC test program.

Based upon the data obtained in this study, the preferred carbon for removing 2,4-DNT and 2,6-DNT from pretreated

Table 8 Summary of Explosives Test Data and Test Results from Air Stripper Stack Testing at the Badger Army Ammunition Plant

Test Data	Air Stripper Stack			Series Average
	1	2	3	
Test Location				
Test Date	3/13/89	3/13/89	3/14/89	
Test Time Period	0902-1310	1352-1758	0807-1342	
Air Stripper Feed Rate (gpm)	4	4	4	
EXPLOSIVES EMISSIONS				
2,4-Dinitrotoluene				
Concentration, lbs/dscf	7.26E-11	9.61E-11	1.26E-10	9.23E-11
Concentration, $\mu\text{g}/\text{m}^3$	1.16	1.54	2.02	1.57
Concentration, ppm/v	1.23E-04	1.63E-04	2.14E-04	1.67E-04
Mass Rate, lb/hr	5.47E-07	7.36E-07	9.59E-07	7.48E-07
2,6-Dinitrotoluene				
Concentration, lb/dscf	1.97E-10	2.90E-10	2.11E-10	2.32E-10
Concentration, $\mu\text{g}/\text{m}^3$	3.15	4.64	3.38	3.72
Concentration, ppm/v	3.34E-04	4.92E-04	3.58E-04	3.95E-04
Mass Rate, lb/hr	1.48E-06	2.22E-06	1.60E-06	1.77E-06

Note: Standard Conditions = 68°F (20°C) and 29.2 inches Hg (760 mm Hg).

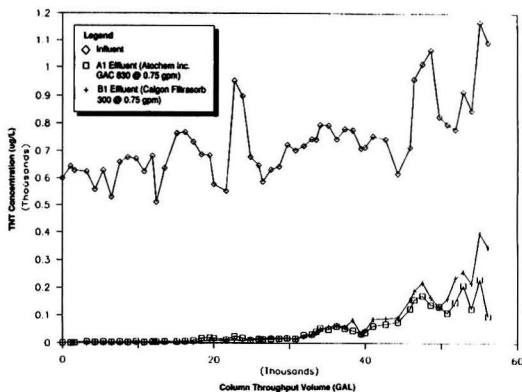


FIGURE 7. TNT Concentration vs. Column Throughput Volume for Test Three at MAAP

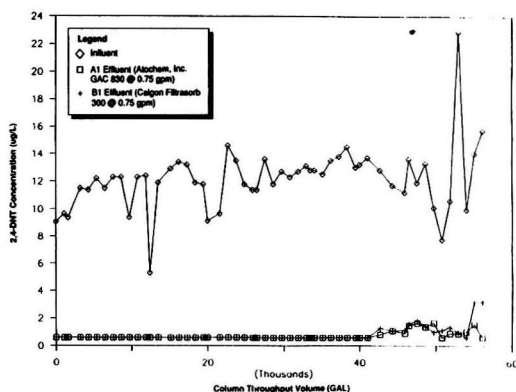


FIGURE 9. 2,4-DNT Concentration vs. Column Throughput Volume for Test Three at MAAP

groundwater at BAAP is Hydrodarc 4000.

Influent and effluent concentrations for Tests One, Two, and Three at MAAP showed that granular activated carbon in continuous-flow columns produced very low effluent concentrations for all nine explosives, generally in the low parts-per-billion (ppb) range during the early portions of each test. These concentrations for RDX, TNT, 2,4-DNT, and 1,3,5-TNB are presented graphically in Figures 7 through 10.

In Test One, columns A1 and B1 both contained Atochem, Inc. GAC 830 but were operated at different influent flow rates (see Table 4). Only RDX exceeded its detection limit of 0.63 $\mu\text{g}/\text{L}$ in column A1's effluent during Test One. This occurred after approximately 8,000 gallons (2,715 bed volumes) of influent, containing an average RDX concentration of 487 $\mu\text{g}/\text{L}$, had passed through the column. When Test One was terminated at a column A1 throughput volume of 10,920 gallons (3,705 bed volumes), the RDX concentration in this column's effluent was 7.05 $\mu\text{g}/\text{L}$.

Test Two had Atochem, Inc. GAC 830 in column A1 and Calgon Filtrasorb 300 in column B1. Both columns were operated at the same influent flow rate (see Table 4). Even after 16,632 gallons (5,644 bed volumes) of influent had passed through both columns, the effluent concentrations of all nine explosives were below their detection limit, which were all approximately 1.0 ppb.

In Test Three, column A1 had Atochem, Inc. GAC 830, and column B1 had Calgon Filtrasorb 300. Both columns were operated at the same influent flow rate (see Table 4). Since the maximum pumping rate for the system was 1.5 gpm, the

flow was split evenly between two sets of columns. Only TNT, RDX, 2,4-DNT, and 1,3,5-TNB exceeded their detection limits in columns A1 and B1 effluents. HMX, Tetryl, 2,6-DNB, 1,3-DNT, and NB were all below their detection limits, even after 56,160 gallons (38,112 bed volumes) of influent had passed through both primary columns (A1 and B1). However, Tetryl, 2,6-DNT, and NB were all below their detection limits in the influent, and HMX's and 1,3-DNB's influent concentrations were low, 3.8 and 4.2 $\mu\text{g}/\text{L}$, respectively.

In Test Three, the average TNT influent concentration was 734 $\mu\text{g}/\text{L}$, and final effluent levels in columns A1 and B1 were 88.6 and 192 $\mu\text{g}/\text{L}$, respectively (see Figure 7). Even though these levels indicate that Atochem, Inc. GAC 830 performed slightly better than Calgon Filtrasorb 300, both carbons performed about the same (see Figure 7) for most of the test. In particular, the apparent breakthroughs for both carbons occurred at approximately the same column throughput volume of 30,000 gallons (20,359 bed volumes). Apparent breakthrough is the point on the breakthrough curve where the concentration of the column effluent first begins to rise above its initial column leakage concentration. The average RDX influent concentration was 549.1 $\mu\text{g}/\text{L}$, and its final effluent levels in columns A1 and B1 were 315 and 344 $\mu\text{g}/\text{L}$, respectively (see Figure 8). As with TNT, the final effluent levels indicate that Atochem, Inc. GAC 830 performed slightly better than Calgon Filtrasorb 300. However, both carbons performed about the same for most of the test; the apparent breakthroughs for both carbons occurred at approximately the same column throughput volume of 12,000 gallons (8,144 bed volumes).

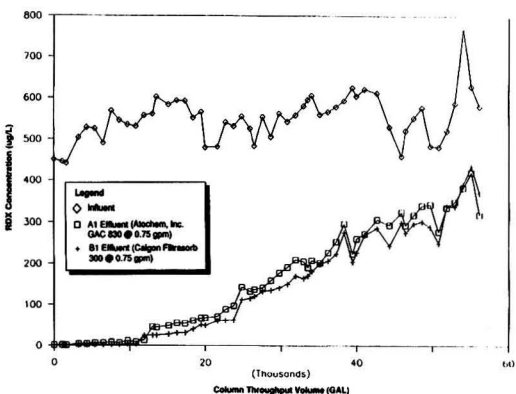


FIGURE 8. RDX Concentration vs. Column Throughput Volume for Test Three at MAAP

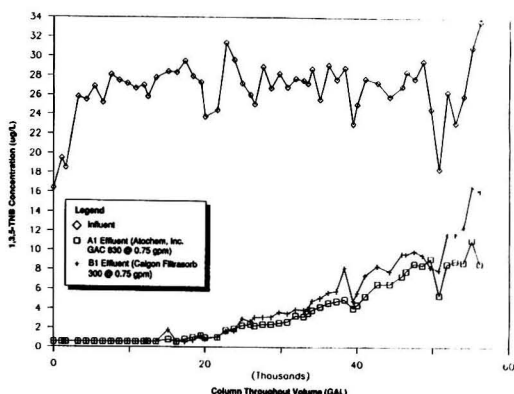


FIGURE 10. 1,3,5-TNB Concentration vs. Column Throughput Volume for Test Three at MAAP

Table 9 Activated Carbon Column Operating and Performance Data for Test Three at the Milan Army Ammunition Plant Atochem, Inc. GAC 830 Versus Calgon Filtrasorb 300

Starting Date: 16 October 1989
 Ending Date: 15 December 1989
 Column Inner Diameter: 4.25 in. (0.354 ft)
 Column Area: 0.0985 ft²
 Bed Volume: 0.197 ft³ (1.47 gal.)

	Atochem, Inc. GAC 830	Calgon Filtrasorb 300
Flow Rate	0.75 gpm	0.75 gpm
Hydraulic Loading	7.6 gpm/ft ²	7.6 gpm/ft ²
Bed Depth	2.0 ft	2.0 ft
Empty-Bed Contact Time	2.0 min.	2.0 min.
TNT Influent Concentration (avg.)	734 µg/L	734 µg/L
RDX Influent Concentration (avg.)	549.1 µg/L	549.1 µg/L
TNT Capacity (rate)*	0.112 lb/lb	0.124 lb/lb
RDX Capacity (rate)*	0.031 lb/lb	0.024 lb/lb
Weight in Carbon in Column	5.1 lb	5.1 lb
Column TNT Capacity (wt)	0.571 lb	0.632 lb
Column RDX Capacity (wt)	0.158 lb	0.122 lb
Total TNT Loading to Column	0.338 lb	0.330 lb
Total RDX Loading to Column	0.191 lb	0.199 lb
TNT Capacity Utilized	59.2%	52.2%
RDX Capacity Utilized	121%	163%
Run Time	54.5 days	54.5 days

*Calculated using isotherm data and average influent concentration.

Figures 9 and 10 present the results for 2,4-DNT and 1,3,5-TNB.

Good agreement was found between the analyses performed by WESTON's Analytic Division and those performed by the WESTON field laboratory for all three tests. Except for TNT and RDX, the analytical results from both WESTON's Analytic Division and the WESTON field laboratory show all explosive concentrations in columns A1 and B1 below their detection limits in all three tests. WESTON's Analytic Division's analytical results for TNT and RDX in columns A1 and B1 were for the most part slightly higher than the WESTON field laboratory's in all three tests. However, the WESTON field laboratory's analytical results for TNT and RDX

in the influent were slightly higher than WESTON's Analytic Division's in Tests Two and Three.

Table 9 summarizes the operating characteristics for Test Three, and Table 10 summarizes the operating characteristics for Atochem, Inc. GAC 830 for Tests One and Two by flow rate. Table 9 shows 59.2% and 52.2% utilization for TNT in columns A1 and B1, respectively. Table 9 also shows 121% and 163% utilization for RDX in columns A1 and B1, respectively. These utilizations of greater than 100% may be attributable to microbiological activity on the carbon surfaces. This activity has been documented in the literature [8-13]. In addition, earlier studies [14] have shown that RDX can be biodegraded, even though it and most explosives are relatively

Table 10 Activated Carbon Column Operating and Performance Data for Atochem, Inc. GAC 830 from Tests One and Two at the Milan Army Ammunition Plant

Column Inner Diameter: 4.25 in. (0.354 ft)
 Column Area: 0.0985 ft²
 Bed Volume: 0.394 ft³ (2.94 gal.)

Flow Rate	0.2 gpm (Test One)	0.7 gpm (Test Two)	1.0 gpm (Test One)
Hydraulic Loading	2.03 gpm/ft ²	7.11 gpm/ft ²	10.15 gpm/ft ²
Bed Depth	4.0 ft	4.0 ft	4.0 ft
Empty-Bed Contact Time	14.7 min.	4.2 min.	2.9 min.
TNT Influent Concentration (avg.)	433 µg/L	508 µg/L	433 µg/L
RDX Influent Concentration (avg.)	487 µg/L	536 µg/L	487 µg/L
TNT Capacity (rate)*	0.080 lb/lb	0.088 lb/lb	0.080 lb/lb
RDX Capacity (rate)*	0.029 lb/lb	0.030 lb/lb	0.029 lb/lb
Weight of Carbon in Column	10.2 lb	10.2 lb	10.2 lb
Column TNT Capacity (wt)	0.816 lb	0.898 lb	0.816 lb
Column RDX Capacity (wt)	0.296 lb	0.306 lb	0.296 lb
Total TNT Loading to Column	0.0076 lb	0.0722 lb	0.0379 lb
Total RDX Loading to Column	0.0086 lb	0.0751 lb	0.0431 lb
TNT Capacity Utilized	0.9%	8.0%	4.6%
RDX Capacity Utilized	2.9%	24.5%	14.6%
Run Time	7.6 days	16.5 days	7.6 days

*Calculated using isotherm data and average influent concentration.

Table 11 Activated Carbon Bed Volumes to Reach TNT and RDX Effluent Levels of Approximately 1 µg/L, 10 µg/L, and 100 µg/L from Test Three at the Milan Army Ammunition Plant

Columns A1 and A2: Atochem, Inc. GAC 830
 Columns B1 and B2: Calgon Filtrasorb 300
 Hydraulic Loading: 7.6 gpm/ft²
 Bed Volume: 0.197 ft³ (1.47 gal.)

TNT

Average Influent Concentration to Columns A1 and B1: 734 µg/L
 Range of Influent Concentration to Column A2: <0.78 to 232 µg/L
 Range of Influent Concentration to Column B2: <0.78 to 397 µg/L

Column A1		Column B1	
Effluent Level (µg/L)	Bed Volumes	Effluent Level (µg/L)	Bed Volumes
0.769	733	1.30	733
10.9	12,093	3.82	12,093
92.1	30,783	92.3	30,050

Column A2		Column B2	
Effluent Level (µg/L)	Bed Volumes	Effluent Level (µg/L)	Bed Volumes
<0.78 ^a	37,745 ^a	<0.78 ^a	37,745 ^a

^aEffluent level and bed volume at end of test.

^bEffluent level and bed volume for first sample taken on 10 November 1989.

Notes: <0.78 = Detection limit of TNT.
 <0.63 = Detection limit of RDX.

resistant to biodegradation. However, no attempt was made in the current study to assess this possibility.

Based on the percent utilizations in Table 9, Calgon Filtrasorb 300 appears to be slightly better for TNT removal. However, since the calculations of these utilizations are based on the extrapolation of limited isotherm test data, one cannot conclude that one carbon is definitely better than the other for removal of TNT and RDX.

Table 10 shows the percent utilizations of Atochem, Inc. GAC 830 at three different hydraulic loadings for TNT and RDX. Even after 7.6 days at the maximum hydraulic loading of 10.15 gpm/ft², percent utilizations for TNT and RDX were only 4.6% and 14.6%, respectively.

Table 11 shows the activated carbon bed volumes required to reach effluent RNT and RDX levels of approximately 1 µg/L, 10 µg/L, and 100 µg/L from Test Three. Based on these results, both Atochem, Inc. GAC 830 and Calgon Filtrasorb 300 appear to be equivalent in meeting the three effluent levels for both TNT and RDX. The results also show that if either columns A1 and A2 or columns B1 and B2 were used as two columns in-series instead of as single columns, a better effluent would be obtained over a longer period of time. The following conclusions were drawn from the two pilot studies:

- Granular activated carbon was capable of removing explosives from contaminated groundwater at two Army Ammunition Plants to 1 µg/L.
- The concurrent removal of 2,4-DNT and 2,6-DNT from groundwater at BAAP using continuous-flow granular activated carbon columns is feasible.
- Based on testing performed in the BAAP study, there is little potential for airborne emissions of 2,4-DNT or 2,6-DNT in the exhaust of an air stripper used to remove volatile compounds.
- The concurrent removal of TNT, RDX, HMX, Tetryl, 2,4-DNT, 2,6-DNT, 1,3-DNB, 1,3,5-TNB, and NB from groundwater at MAAP using continuous-flow granular activated carbon is feasible.

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Evaluation of a Hydraulically-Installed Suction Lysimeter to Obtain Representative Soil Water Samples

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The existing technology for obtaining liquid from the vadose zone involves drilling a bore hole, introducing a silica slurry packing, inserting a sampling device, and backfilling the hole. The high cost of drilling and backfilling contribute to the considerable expense of this procedure. Moreover, drilling through potentially contaminated soil increases the possibility of expanding the area of contamination. In this study, a novel small diameter suction lysimeter with a porous ceramic section was designed and tested. The stainless steel ram-tipped lysimeter was designed to be installed into the ground using a hydraulic ram without the need of drilling a bore hole, thereby reducing the expense and potential for cross-contamination. Simulated field testing was employed to evaluate the performance of the hydraulically-installed lysimeter as compared to a lysimeter installed using the standard silica slurry packing technique. The decrease in sample volume uptake due to plugging in the pores of the ceramic section was investigated for the lysimeters installed both hydraulically and with the silica slurry packing, in three types of soil: medium sand, silty clay, and a clayey topsoil-medium sand blend. The soil moisture operating range for the lysimeters was ascertained in a test chamber filled with a blend of clayey topsoil and medium sand. An investigation of the effect of sampling on the concentration of solutes was performed with aqueous solutions of ethanol and phenol.

INTRODUCTION

The vadose zone is defined as the unsaturated area located between ground level and the groundwater table. The vadose zone is characterized by the presence of solid, liquid, and vapor phases. Chemical spills [1], underground storage tank leaks [2], and improper burial of materials [3] have the potential to cause extensive vadose zone and groundwater contamination. Liquids are transported downward through the soil by percolation and gravitation forces, and upward and laterally as a result of capillary action. Vapors are conveyed through the soil due to concentration and temperature gradients. Lateral movement of liquids and vapors is generally limited. The transport of both liquids and vapors is facilitated, however, by the presence of fractures or channels.

To ascertain the extent of underground pollution and the potential for groundwater contamination requires monitoring in the vadose zone. Samples of the vapor phase are usually collected by a vapor probe, a long tube which is installed vertically to a particular depth [2]. Suction lysimeters are used to collect liquid samples from the vadose zone. The lysimeter sampling apparatus consists of a hollow porous section that is maintained at vacuum. Liquid is transported into the ly-

simeter due to the pressure differential across the porous section. The flow of liquid through the porous section is sustained by maintaining a pressure differential which is finite yet below the entry capillary pressure. The performance of suction lysimeters is restricted by the physical and chemical properties of the porous section. The porous section may be categorized by the type material, pore size distribution (or permeability), surface area, degree of hydrophilicity, and surface adsorption characteristics.

The existing technology for obtaining liquid from the vadose zone involves drilling a bore hole (usually four inches in diameter), injecting a silica slurry packing into the bottom of the hole, inserting a lysimeter sampling device, and backfilling and plugging the hole [4]. This procedure is expensive due to the high cost of drilling and backfilling the well. Furthermore, the potential for cross-contamination is exacerbated by drilling a conduit through potentially contaminated soil. In this work, a new lysimeter design, approximately one inch in diameter, capable of being hydraulically installed at desired depth without drilling, was evaluated. The results of this study will be used to improve the operation and lower the cost of sample collection in the vadose zone using suction lysimeters.

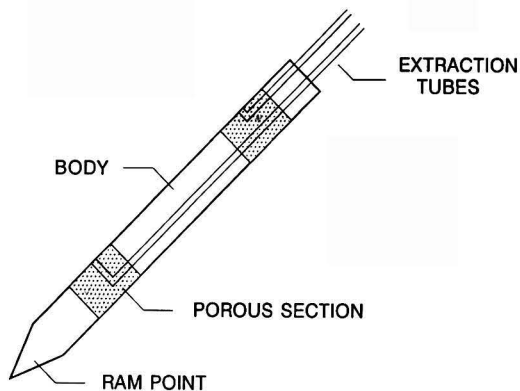


FIGURE 1. Schematic diagram of suction lysimeter.

DESIGN AND OPERATION

The suction lysimeter was designed to be installed into the vadose zone with a hydraulic ram. This design eliminates the need to drill and backfill a bore hole. A schematic diagram of the hydraulically-installed suction lysimeter is shown in Figure 1. The lysimeter is comprised of a stainless steel ram point and body, one or more ceramic porous sections, and one or more extraction tubes. The stainless steel ram point was designed to promote the installation of the lysimeter into the test soils by a hydraulic ram. Liquid present in the vadose zone may be drawn into the lysimeter through the porous section by application of negative pressure on the extraction tubes. The liquid samples are transported to collection vessels at the surface via the extraction tubes.

The porous section of the suction lysimeter can be modeled as a collection of capillary tubes operating in parallel with each other. In saturated soil, liquid enters each capillary tube and is transported to the interior of the lysimeter. In unsaturated soils, however, soil vapor may infiltrate the capillary tube and displace the liquid. If vapor occupies the entire capillary tube, the lysimeter will preferentially collect vapor and severely limit the sampling of liquids. The pressure at which vapor enters the pores is known as the bubble pressure or capillary entry pressure, P_E , and may be described by the following equation for a porous medium of uniform pore size [5].

$$P_E = \frac{4\gamma \cos\theta}{D_i} \quad (1)$$

where γ is the surface tension of the liquid, θ is the angle of contact between the liquid and the surface of the solid porous material, and D_i is the pore diameter. The capillary entry pressure limits the operating range of the suction lysimeter by establishing a maximum suction pressure for a particular pore diameter. For example, to obtain an aqueous sample at 20°C ($\gamma = 72.8$ dynes/cm) from unsaturated soil by a hydrophilic porous section ($\theta = 0^\circ$) it is essential that the maximum pore diameter of the porous section be less than 2.87 μm .

EXPERIMENTAL

Experimental testing of the hydraulically-installed suction lysimeters was performed at the Institute of Gas Technology's Vadose Zone Testing Facility. The lysimeters were evaluated in terms of bubble pressure, pore plugging, soil moisture operating range, and representative sampling.

Table 1 Soil Characteristics

Soil Type	Median Particle Size (μm)	Specific Gravity	Organic Content (%)
Median Sand	500	2.65	0.0
Silty Clay	6	2.72	6.1
Clayey Topsoil	4	2.70	6.3

Bubble Pressure Tests

Bubble pressure tests were performed on each lysimeter to determine the capillary entry pressure of the porous section. To test for leaks, the lysimeter was submerged into a transparent container filled with distilled water and was pressurized with nitrogen. Suction was then applied to the extraction tube and 0.5 L of water was drawn into the lysimeter. Suction was discontinued and the extraction tube was gradually pressurized with nitrogen. The bubble pressure, defined as the pressure at which bubbles begin to form on the exterior surface of the porous section of the lysimeter, was recorded.

Pore Plugging Tests

Pore plugging tests were performed using four lysimeters, two installed hydraulically and two using a standard silica slurry packing, in saturated test soils. Three soil types were obtained for use in the pore plugging and soil moisture operating range tests. STS Consultants Ltd. (Northbrook, IL) performed a combined sieve hydrometer analysis following ASTM D-422 procedures and an organic content test following ASTM D-2974 for the three soils described as medium sand, silty clay, and clayey topsoil. A summary of the median grain size, specific gravity, and organic content is given in Table 1, and the grain size distribution is shown in Figure 2. Upon consultation with soil scientists at the U.S. Department of Agriculture (USDA), it was recommended that a blend of 75% clayey topsoil with 25% medium sand would yield a soil with intermediate permeability representative of "typical" topsoil. Therefore, based on the soil analyses and USDA recommendation, the composition of the three test soils were: (1) 100% medium sand; (2) 100% silty clay; and (3) a 75% clayey topsoil-25% medium sand blend.

Three 200 L polyethylene (PE) drums, each filled with one of the three different test soils, were used for evaluating pore plugging in the suction lysimeters. The system configuration

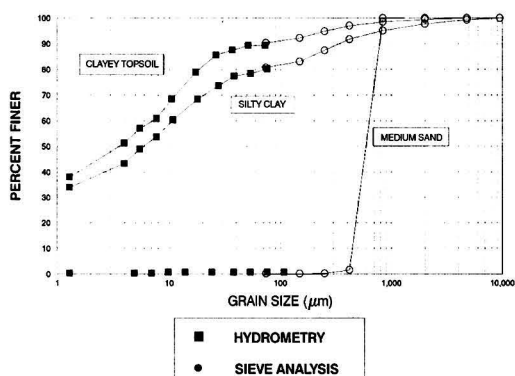


FIGURE 2. Grain size distribution for soil types

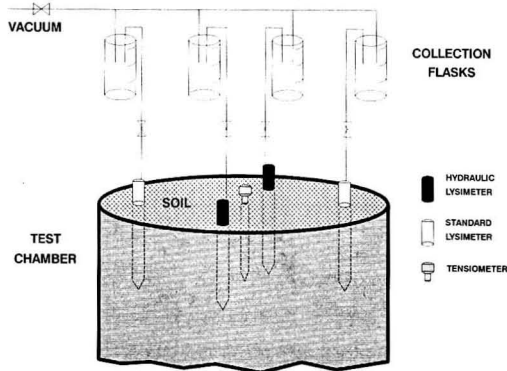


FIGURE 3. Schematic diagram of pore plugging test apparatus.

consisted of a large capacity vacuum pump connected to each of four collection flasks fabricated from translucent, 10 cm diameter, polyvinylchloride (PVC) pipes with sealed PVC end caps. The four 12 L collection flasks, graduated in 1 L intervals to facilitate volume measurement, were connected to the four suction lysimeters (Figure 3). The moisture content of the test soil was measured by a tensiometer (Model 2725 Jet Fill, Soilmaster Equipment Corp., Santa Barbara, CA) inserted into the center of the test chamber.

The following protocol was used for preparing the soil in the test chambers. The soil was packed into each test chamber to a depth of 30 cm in intervals of 15 cm, and the soil was hand tamped after each interval. To accommodate the silica slurry packing, two 10 cm diameter PVC casings were placed on top of the soil at the desired location in the sample chamber (Figure 3). The silica slurry, composed of 500 g of 200 mesh silica flour (Soilmaster Equipment Corp.) in 0.15 L distilled water, was poured into the PVC casing to a depth of approximately 10 cm. For the standard installation, each of two lysimeters was inserted into the silica slurry in the center of the PVC casing. Additional silica slurry to cover the porous cup section of the lysimeter was poured into the casing. The remainder of the soil was added to the test chamber to the same depth as the silica slurry at 15 cm intervals. The PVC casings were carefully removed and the sample chamber was completely filled with soil, hand tamped every 15 cm. Two additional lysimeters were installed using a hydraulic ram into the test soil to the same depth as the standard lysimeters. To measure the soil suction, a tensiometer was installed at the center of the test chamber at the same depth as the lysimeters. The test soil was thoroughly saturated with water and allowed to equilibrate overnight.

Pore plugging was evaluated by applying suction to the four 12 L collection flasks, each of which was connected to a lysimeter. After five hours the suction was discontinued and the water drawn from the soil by each lysimeter was measured. The test was repeated until the incremental volume of water obtained from each lysimeter reached a plateau value.

Soil Moisture Operating Range Tests

The soil moisture operating range test chamber consisted of a PE drum (1100 L) filled with test soil. The configuration of the vacuum and collection apparatus was similar to that of the pore plugging system, consisting of the large capacity vacuum pump and four 12 L collection flasks. The operating range apparatus included a series of extraction plates (Model 1950, Soilmaster Equipment Corp.) and extraction tubes (Model 1900, Soilmaster Equipment Corp.) used to reduce the moisture content of the test soil (Figure 4).

Soil moisture operating range was evaluated for the clayey topsoil-medium sand blend using four lysimeters; two installed hydraulically and two with a standard silica slurry packing. Preparation of the test soil in the test chambers and installation of the lysimeters followed the procedure previously described for the pore plugging tests. The test soil was thoroughly saturated with water and allowed to equilibrate for two weeks with the periodic addition of water. To control the suction pressure in the test soil, two extraction plates were buried near the bottom of the test chamber and five extraction tubes were inserted into the test soil (Figure 4). Soil suction was measured by a series of five tensiometers, installed in the test chamber to the same depth as the lysimeters.

The lysimeter operating range was evaluated by applying suction to four 12 L graduated, collection flasks, each of which was connected to a lysimeter. After one hour, suction was discontinued and the volume of water collected by each lysimeter was measured. The soil moisture content was subsequently decreased by removing water from the test chamber via the extraction plates and tubes. The soil suction pressure was permitted to equilibrate over a period of twenty-four hours and the one hour operating range test was repeated for progressively higher soil suction pressures (lower soil moisture content).

Representative Sampling Tests

Sample representativeness was evaluated for aqueous solutions of ethanol and phenol, varying from 0.5 to 10 g/L. A suction lysimeter was inserted into each standard solution and was used to transfer a sample of approximately 0.5 L to a collection flask. The hydrocarbon concentration of the extracted sample was compared to that of the original solution by total organic carbon (TOC) analysis.

RESULTS AND DISCUSSION

Bubble pressure tests were performed on each suction lysimeter to detect hairline cracks in the porous section and to ensure that the capillary entry pressure had a tolerance range of $\pm 5\%$. After replacing several of the porous ceramic sections, sixteen lysimeters with bubble pressures equal to 117 ± 5 kPa were obtained. The relationship between capillary entry pressure and pore diameter (Eq. 1) establishes that a pressure of 117 kPa corresponds to a pore diameter of 2.5 μm . This

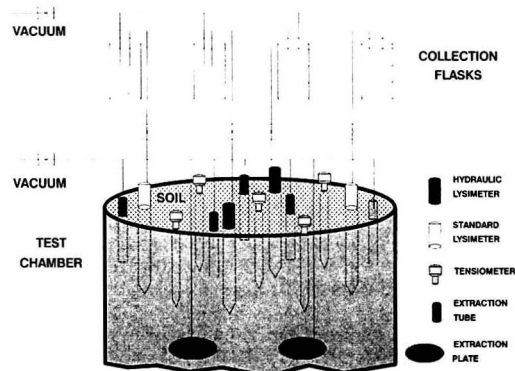


FIGURE 4. Schematic diagram of soil moisture operating range test apparatus.

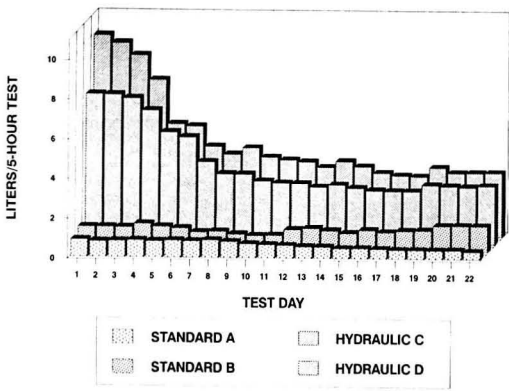


FIGURE 5. Results of pore plugging test in medium sand test soil.

value correlates with the maximum pore diameter of $2.4 \mu\text{m}$ derived from mercury porosimetry of the porous ceramic section.

Pore plugging experiments were carried out in three different saturated test soils: medium sand, silty clay, and a 75% clayey topsoil-25% medium sand blend. Figure 5 shows the volume of liquid collected during each 5-hour test over the complete test period for the medium sand test soil. At the start of the experiment, the volume of water collected by the hydraulically-installed lysimeters (labeled C and D) was approximately 10 times that collected from the lysimeters (labeled A and B) installed by the standard method using the silica slurry packing. Pore plugging in the ceramic section of the lysimeters resulted in a decrease in the volume of water collected during subsequent 5-hour test periods. At the conclusion of the 21-day test period, the volume of water collected by the lysimeters had reached a plateau value, with the exception of lysimeter B which exhibited anomalous results. For the hydraulically-installed lysimeters C and D, the volume of water was reduced by an average of 65% over the complete test period. The lysimeter A installed with the silica slurry packing showed a decrease of 55% over the same time period. The larger sample volumes collected by the lysimeters C and D demonstrate the advantage of hydraulic installation for soils similar to the medium sand test soil.

The results of the pore plugging experiments in the silty clay test soil are shown in Figure 6. Contrary to the results in the medium sand test soil, the hydraulically installed lysimeters collected a significantly smaller volume of water than the lysimeters installed using the standard silica slurry packing. The

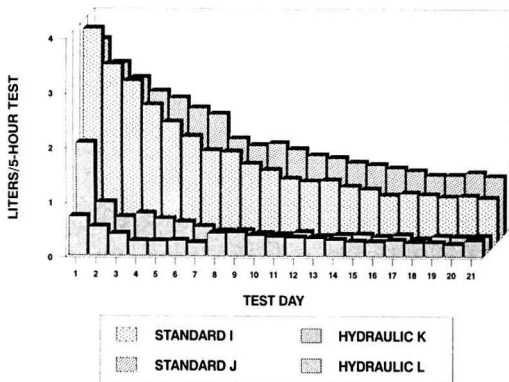


FIGURE 6. Results of pore plugging test in silty clay test soil.

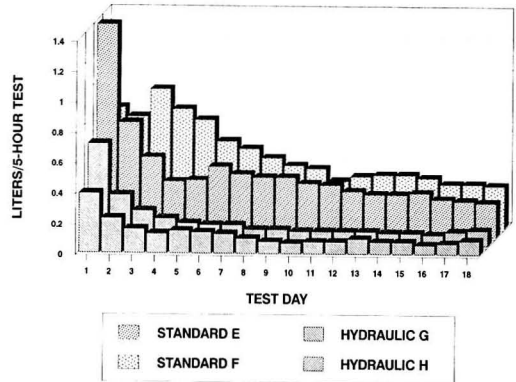


FIGURE 7. Results of pore plugging test in 75% clayey topsoil-25% medium sand test soil.

smaller uptake of sample by the hydraulically-installed lysimeters may be a consequence of the relatively small particle size of the silty clay test soil and thus, its increased ability to plug the pores of the ceramic section. The silica slurry packing shields the porous ceramic section from intimate contact with the soil and therefore, these lysimeters operate at a higher efficiency. All four of the lysimeters, however, exhibited a marked decrease in the sample volume collected over the period of the test.

Results similar to the pore plugging in the silty clay test soil were obtained using the clayey topsoil-medium sand test soil (Figure 7). The relatively small particle size of the topsoil produced a larger degree of pore plugging in the ceramic section of the hydraulically-installed lysimeters. Furthermore, the volume of water collected in the clayey topsoil-medium sand was significantly less than the volume collected in the silty clay. This data further corroborates the concept that the particle size of the soil strongly influences the degree of pore plugging.

A comparison of the collection rate at the completion of the pore plugging test in the three test soils is shown in Figure 8. The rates of collection at the completion of the test illustrate the differences in the sample volume which could be obtained from different soils over a prolonged sampling period. In terms of a 24-hour daily collection rate at the completion of the plugging test, the hydraulically installed lysimeters collected liquid at a rate of 14.7, 1.2, and 0.5 liters per day for the medium sand, silty clay and clayey topsoil-medium sand test soils, respectively. For comparison, the lysimeters installed with the silica slurry collected liquid at a rate of 4.0, 4.4, and

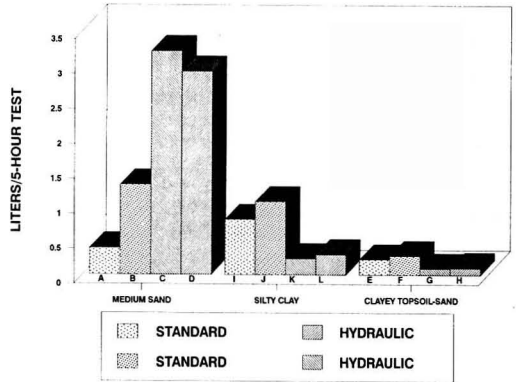


FIGURE 8. Comparison of pore plugging tests in three test soils.

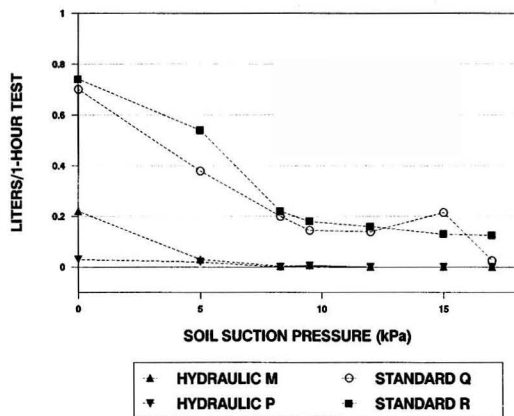


FIGURE 9. Results of soil moisture operating range test in 75% clayey topsoil-25% medium sand test soil.

1.2 liters per day. Although the hydraulically-installed lysimeters collected smaller volumes in two of the three test soils, these volumes were more than adequate to meet the need for monitoring and analysis on a daily basis.

Soil moisture operating range experiments were performed in the clayey topsoil-medium sand test soil to determine the extent of any restrictions in the function of the lysimeters in unsaturated soils. The soil suction pressure is the conventional mode of indicating the degree of soil pressure, with 0 kPa corresponding to a completely saturated soil. Unfortunately, the soil suction pressure is not linearly proportional to the moisture content in the soil. Furthermore, the relationship varies depending on the composition of the soil. Moisture analysis of the completely saturated clayey topsoil-medium sand blend by weighing and drying yielded a soil water content of 27.0%.

The volume of water collected by the lysimeters as a function of the soil suction pressure is shown in Figure 9. The data indicate that the hydraulically-installed lysimeters collected a negligible volume of liquid when the soil suction pressure was greater than 5 kPa. The lysimeters installed with the silica slurry packing continued to extract liquid samples from the soil at a soil suction pressure of 17 kPa (17.7% moisture). It is suggested that the limited capacity of the hydraulically-installed lysimeters is a result of a possible break in contact of the porous ceramic section with the soil as the soil gets progressively drier [6], as well as a decrease in the efficiency of the porous section due to pore plugging. It is possible that contact would be maintained and samples obtained at high soil moisture pressures if the lysimeter were hydraulically installed into a soil of low moisture content.

Representative sampling tests were performed to determine whether the concentration of organic compounds extracted by the suction lysimeter was representative of the original solution. These tests were used to assess the degree of adsorption onto the porous ceramic, as well as the possibility of loss through the vacuum system. The results of the representative sampling tests for single extractions of aqueous ethanol and phenol solutions are given in Table 2. The data indicate that for the compounds and their concentration range used in this study the lysimeter collected a representative sample of the solution. Additional analysis using lower concentration solutions in which the lysimeter is inserted into a test soil would be required to further corroborate these results.

CONCLUSIONS

A novel, hydraulically-installed suction lysimeter for obtaining liquid samples from the vadose zone was designed and

Table 2 Lysimeter Sampling of Aqueous Solutions

Compound	Solution Concentration (g/L)		Percent Deviation
	Original	Extracted	
Ethanol	10.00	9.14	91
	5.00	4.84	97
	2.50	2.47	99
	1.00	0.97	97
	0.50	0.59	118
Phenol	10.00	8.97	90
	5.00	3.53	71
	2.50	2.65	106
	1.00	1.06	106
	0.50	0.44	88

tested. It was demonstrated that the suction lysimeter could be installed using a hydraulic ram, thus eliminating bore hole drilling and silica slurry packing. The results of pore plugging experiments demonstrate a relationship between the pore size of the ceramic section and the particle size of the soil. The larger size sand did not plug the pores of the ceramic section and the flow rate into the hydraulically-installed lysimeter was higher than into the lysimeter with the silica slurry packing. Conversely, the topsoil-sand and clay soils markedly decreased the flow of liquid into the hydraulically-installed lysimeter. However, these volumes obtained from all three test soils by the hydraulically-installed lysimeters were far in excess of the amount required for monitoring and analysis on a daily basis. The soil moisture operating range tests in topsoil-sand blend showed that the hydraulically-installed lysimeters were limited in operation to a soil suction pressure of approximately 5 kPa, while those lysimeter installed with the silica slurry packing collected samples at pressures up to 17 kPa. Current work is being done to improve the pore size distribution of the ceramic section for operation in low moisture environments.

ACKNOWLEDGMENTS

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Ultrasonic Destruction of Chlorinated Compounds in Aqueous Solution

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The application of ultrasonic-wave energy for the destruction of low concentrations of carbon tetrachloride into nonhazardous end products is described, and the results of experimental work are presented. Process parameters studied included steady-state temperature, concentration, pH, irradiation time, and the intensity of the applied ultrasonic-wave energy. Greater than 99% destruction efficiencies were achieved through this process, and the irradiation time required for a given degree of destruction decreased with increasing intensity of the ultrasonic energy. In addition, a detailed chemical reaction mechanism for the destruction of carbon tetrachloride in water was formulated. The agreement between the model and experimental results is generally good.

INTRODUCTION

Chemical ultrasonics began in 1927 when Richards and Loomis reported the acceleration of conventional reactions and the redox process by ultrasound [1]. Since then, a number of chemical reactions have been observed in an ultrasonic field [2-4]. In recent years, attention has focused upon the application of ultrasonic energy to problems associated with water pollution, especially in removing toxic and hazardous organic compounds from contaminated water [5, 6]. Removal of these compounds may be difficult and costly if very low concentration levels must be achieved. For many contaminants, the ultrasonic process has the advantage of completely destroying or converting these organics, not simply transferring them to another medium.

The chemical effects of ultrasound are due to the phenomenon of acoustic cavitation [7]. Sound is transmitted through any fluid as a wave consisting of alternating compression and rarefaction cycles. If the rarefaction wave is sufficiently powerful, it can develop a negative pressure large enough to overcome the intermolecular forces binding the fluid. As a result, the molecules are torn apart from each other and form tiny microbubbles. These microbubbles gradually grow during the compression/rarefaction cycles until they reach a critical size. Subsequent compression then causes the microbubbles to col-

lapse almost instantaneously, thereby releasing a large amount of energy. Temperatures of the order of 5000 K have been experimentally obtained [8], and pressures of the order of 1000 atmospheres have been calculated [9].

The primary chemical reactions result, therefore, from the transient state of these high pressures and temperatures, both during and immediately after collapse of the microbubbles [10, 11]. Solvent and solute vapors in the cavity undergo direct thermal dissociation to yield CO₂, H₂O, and radicals, such as hydroxyl and atomic hydrogen. Some of these radicals may recombine to form new compounds. In the bulk liquid phase, secondary reactions between solute molecules and radicals generated in the cavities also take place. These two reaction schemes together are responsible for the chemical effect of ultrasonics upon the solution.

In this paper, we present the results of an investigation of the ultrasonic irradiation of carbon tetrachloride in laboratory-simulated groundwater at various pH values, temperatures, and power intensities. Kinetic data and selected chemical mechanisms are discussed and proposed. To study oxidant efficiency, chemical oxidants, such as hydrogen peroxide, are also considered. This work is part of a project entitled "Ultrasonic Process for Detoxification of Groundwater and Soil," sponsored by the U.S. Department of Energy, Office of Technology Development, to develop an innovative process for the effective destruction of chlorinated organics in soil and groundwater.

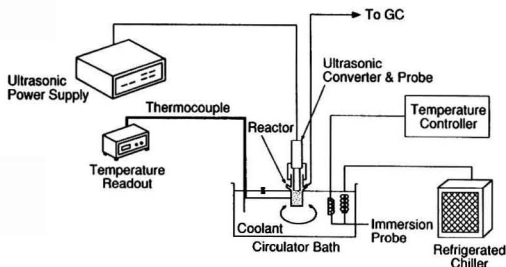


FIGURE 1. Experimental Apparatus

EXPERIMENTAL CONSIDERATIONS

Reaction Apparatus

Irradiations were carried out with an ultrasonic power supply (Sonics & Materials, VC 600) with a continuously variable output from 0 to 600 W, operating at 20 kHz. Figure 1 shows the schematic diagram of the experimental apparatus, and Figure 2 shows a close-up of the reaction cell. The ultrasonic intensity at the titanium tip of the sonication probe was about 27 W/cm². The sonication vessel was a borosilicate glass cell with a stainless steel collar, which could be screwed onto the horn of the ultrasonic probe so that the probe could be immersed into the sample solution as sonication proceeded. The reaction vessel had side arms so that an oxidant, such as hydrogen peroxide, could be introduced into the reactor, and gas samples could be directed to a gas analysis system.

The temperature inside the reaction vessel was kept relatively constant by circulating cooling water in a constant-temperature bath, which was continuously monitored by a thermocouple probe and temperature readout. An alternative ultrasonic power supply (Sonics & Materials, VC 60) was used to study the effect of power intensity upon the destruction of organics. The major improvement of this apparatus is the addition of a wattmeter, which displays the actual, instantaneous ultrasonic power delivered into the sample solution. In this way, converter and probe losses can be automatically deducted so that the effect of power intensity can be accurately investigated.

Materials

Carbon tetrachloride (CCl₄), sulfuric acid (certified ACS

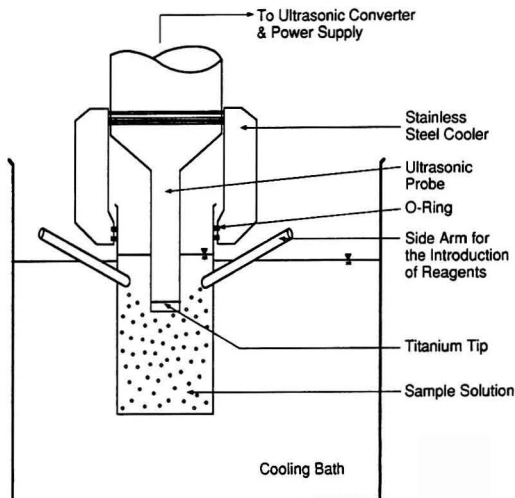


FIGURE 2. Sonication Cell

grade, Mallinckrodt, Inc.), hydrogen peroxide (30%, analytical grade, Mallinckrodt, Inc.) and n-hexane (certified for trace environmental analysis by capillary GC & GC-MS, Bardick & Jackson) were used as received by the suppliers. Sodium sulfate (certified ACS grade, Mallinckrodt, Inc.) was washed by n-hexane to remove trace impurities and was dried in an oven (104°C) overnight before it was used. A standard CCl₄ solution was prepared by stirring the neat liquid with laboratory deionized water overnight and was equilibrated for at least 24 hours. This standard solution was then used to prepare all of the sample solutions for the subsequent experiments.

Analytical Method

Analysis of CCl₄ was carried out by a gas chromatograph equipped with an electron capture detector. A glass column packed with a 80/120 Carbowax B/3%, SP-1500 stabilizer was used after it had been conditioned at 230°C for more than 15 hours. Immediately following the experiment, irradiated sample solutions were extracted with n-hexane and were dehydrated by sodium sulfate before being analyzed. The pH value of the sample solution in the pH-effect study was determined by using a Cole-Parmer Chemcadet pH/ion/mv meter (model 5986-50), which was calibrated with standard solutions of pH 4, 7, and 10 before use.

Experimental Procedures

A 15-mL sample solution, which was diluted from the standard CCl₄ solution, was prepared for each experiment and was irradiated for a desired length of time. The power intensity delivered into the solution was regulated by a controller on the power supply panel. The temperature inside the reactor was monitored continuously throughout the experiment. After sonication ceased, the irradiated solution was extracted, dehydrated, and then stored in a Teflon-sealed sampling bottle for future treatment or analysis.

CHEMICAL KINETIC MECHANISM AND MODEL DEVELOPMENT

The chemical mechanism presented in Table 1 was developed by systematically considering the major plausible elementary reactions of water, dissolved air (nitrogen and oxygen), organics (CCl₄), and their related reactions in the field of ultrasonics [12-14]. The reactions are initiated by the dissociation of water molecules in the collapsing cavitation holes (the 'Hot Spot') (Eq. 1). Atomic hydrogen (H) and hydroxyl radicals (OH) are formed through this reaction. These two radicals recombine to form water or hydrogen molecules (H₂), or they react with oxygen molecules (O₂) to yield hydroperoxide radicals (HO₂) and hydrogen peroxide (H₂O₂) (Eqs. 2 to 6). These radicals further react with the H₂O₂ produced in these reactions to form H₂ molecules, water, and other radicals (Eqs. 7 to 10). In order to simplify the treatment, we will not consider here the secondary reactions of H and OH with the H₂O₂ that is formed in the system.

In the presence of dissolved nitrogen, nitrogen molecules (N₂) decompose in the collapsing cavitation holes (Eq. 11) to form atomic nitrogen (N). Following a series of reactions, N then reacts with the OH radicals produced from the dissociation of water and related reactions to yield nitrate and nitrite (Eqs. 12 to 15). Atomic nitrogen also reacts with H and O₂ molecules to regenerate N₂ and H₂ molecules and to produce nitric-oxide (NO) and O₂ radicals (Eqs. 16 to 18).

Oxygen molecules dissolved in the water also decompose in the cavitation holes (Eq. 19) to produce atomic oxygen (O) and compete with H in Eq. 2, leading to the formation of

Table 1 Proposed Chemical Kinetic Mechanism

- A. Water Dissociation:
- $\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$
 - $\text{H} + \text{H} \rightarrow \text{H}_2$
 - $\text{H} + \text{O}_2 \rightarrow \text{HO}_2$
 - $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$
 - $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$
 - $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$
 - $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{H}_2\text{O}$
 - $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2 + \text{HO}_2$
 - $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$
 - $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$
- B. In the Presence of Nitrogen:
- $\text{N}_2 \rightarrow 2\text{N}$
 - $\text{N} + \text{OH} \rightarrow \text{NO} + \text{H}$
 - $\text{NO} + \text{OH} \rightarrow \text{HNO}_2$
 - $\text{NO} + \text{OH} \rightarrow \text{NO}_2 + \text{H}$
 - $2\text{NO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{HNO}_2 + \text{HNO}_3$
 - $\text{N} + \text{H} \rightarrow \text{NH}$
 - $\text{NH} + \text{NH} \rightarrow \text{N}_2 + \text{H}_2$
 - $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$
- C. In the Presence of Oxygen:
- $\text{O}_2 \rightarrow 2\text{O}$
 - $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$
 - $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$
 - $\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$
 - $\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{HO}_2$
- D. In the Presence of Organics (CCl_4):
- $\text{CCl}_4 + \text{OH} \rightarrow \text{products}$
 - $\text{CCl}_4 + \text{H} \rightarrow \text{products}$
 - $\text{CCl}_4 + \text{HO}_2 \rightarrow \text{products}$
 - $\text{CCl}_4 + \text{O} \rightarrow \text{products}$
 - $\text{CCl}_4 \rightarrow \text{products}$

hydroxyl radicals (Eq. 20). Atomic oxygen then reacts with H_2 molecules, H_2O_2 , and HO_2 to form O_2 molecules and other radicals, such as H and OH (Eqs. 21 to 23).

The target contaminant, CCl_4 , present in the water is either directly decomposed in the cavities (Eq. 28) or oxidized by radicals (Eqs. 24 to 27). If the reaction does not proceed to completion, the final products of the irradiation of CCl_4 by ultrasound are water, carbon dioxide, and/or some other chemical compounds.

On the basis of the chemical reaction mechanism proposed above, the primary pathway appears to be the thermal dissociation in the collapsing cavitation holes, such as those represented in Eqs. 1, 11, 19, and 28. The high temperatures and pressures created during cavitation provide the activation energy required for the bond cleavage. Water, nitrogen, oxygen, and carbon tetrachloride molecules decompose in these cavities to directly form the radicals. These radicals then either react with each other to form new molecules and radicals or diffuse into the bulk liquid to serve as oxidants. The secondary reaction seems to be in the bulk-liquid phase, where CCl_4 and other molecules are oxidized by oxidants, such as the radicals generated in the cavities.

Therefore, to better clarify these reactions, the whole system can be divided into two major areas: (1) the collapsing cavitation holes, in which molecule vapors may reach supercritical conditions and decompose, and (2) the bulk-liquid phase under normal operating temperatures and pressures, in which molecules are oxidized by radicals to form new products. In a batch reactor with reactions undergoing the bulk-liquid phase, we assume a second-order rate constant, in which the destruction rate of CCl_4 can be represented by the following equation:

$$-d[\text{CCl}_4]/dt = k_{24}[\text{OH}][\text{CCl}_4] + k_{25}[\text{H}][\text{CCl}_4] + k_{26}[\text{HO}_2][\text{CCl}_4] + k_{27}[\text{O}][\text{CCl}_4] \quad (1)$$

The rate of disappearance of CCl_4 equals the sum of the rates of all of the related reactions in the mechanism. If the reaction takes place in the cavitation holes, it is reasonable to assume a second-order rate constant again. In this case, the destruction rate of CCl_4 can be expressed by a rate formula:

$$-d[\text{CCl}_4]/dt = k_c * k_{28}[\text{CCl}_4][\text{M}] \quad (2)$$

where M is any collision partner and k_c is the system adjustment coefficient, which is a function of bubble concentration, bubble radius, mixing extent of the system, etc. This coefficient is assumed to be a constant if all of the experimental conditions, such as reaction vessel size, steady-state temperature, and power intensity, are unchanged. This coefficient can be obtained by a best fit of the experimental data into the model. Because the reaction occurs in the collapsing cavitation holes, $[\text{CCl}_4]$ in rate formula (2) represents the concentration of CCl_4 in the vapor phase. If we assume an ideal gas and Rault's law to hold, this value can be estimated by Henry's law.

Hence, in addition to CCl_4 , the net reaction rates for all the other compounds in the system can also be expressed in similar rate formulas, or differential equations, that describe the decreasing or increasing rates in the field of ultrasonics. If all of the reaction rate constants are available, these differential equations could be solved simultaneously to obtain the individual concentration profile for each species as a function of irradiation time.

RESULTS AND DISCUSSION

Exposure of CCl_4 solutions to ultrasound in the presence of dissolved air results in a decrease of the $[\text{CCl}_4]$ in the solutions. Greater than 99% removal efficiency was obtained in the current experiment. Figures 3, 4, and 5 show the plot of $[\text{CCl}_4]$ versus sonication time at various initial $[\text{CCl}_4]$. Initial $[\text{CCl}_4]$ as high as 130 ppm (Figure 3) dropped to about 5 ppm after

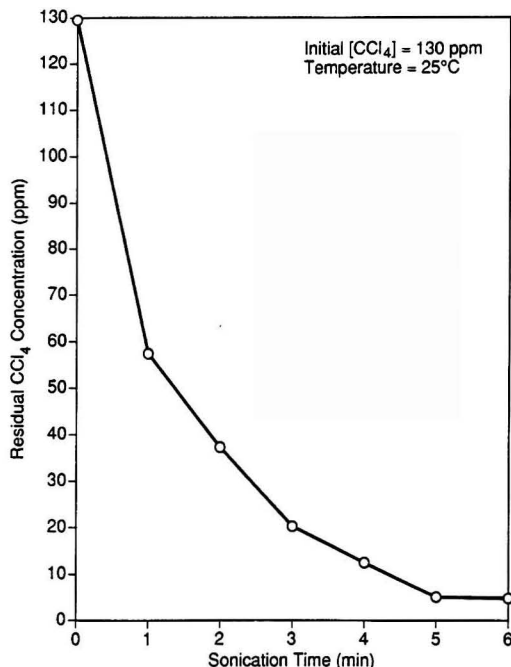


FIGURE 3. $[\text{CCl}_4]$ Decrease Versus Sonication Time; $[\text{CCl}_4] = 130$ ppm

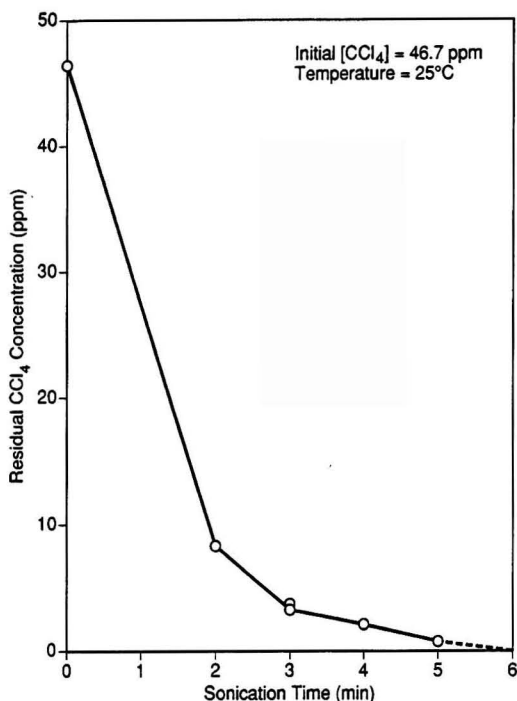


FIGURE 4. $[\text{CCl}_4]$ Decrease Versus Sonication Time; $[\text{CCl}_4] = 47 \text{ ppm}$

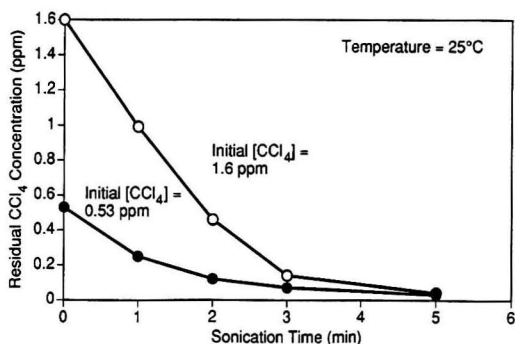
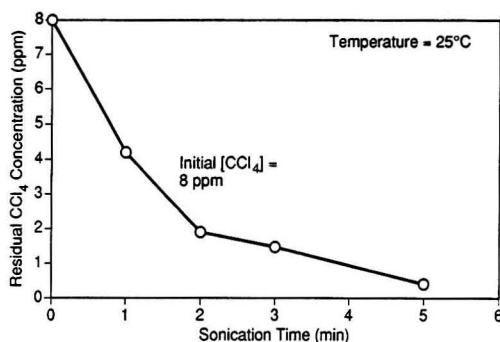


FIGURE 5. $[\text{CCl}_4]$ Decrease Versus Sonication Time; $[\text{CCl}_4] = 8 \text{ ppm}, 1.6 \text{ ppm}, 0.53 \text{ ppm}$

6 minutes of irradiation, while initial $[\text{CCl}_4]$ of 1.6 ppm (Figure 5) dropped to about 0.05 ppm at the same irradiation time. The concentration of residual CCl_4 decreased exponentially with sonication time. With higher initial $[\text{CCl}_4]$ within the same sonication period, greater decreases in residual CCl_4 were observed; however, the destruction efficiency was about the same. First-order plots of $\ln[\text{CCl}_4]$ versus sonication time for various initial $[\text{CCl}_4]$ are shown in Figure 6. The ultrasonic degradation of $[\text{CCl}_4]$ apparently followed first-order kinetics within the current experimental concentration range. An average first-order rate constant of $k = 0.7 \text{ min}^{-1}$ was determined from the slopes of these plots. It has been reported [15] that at low $[\text{CCl}_4]$, CCl_4 destruction should follow a first-order reaction, but at higher concentrations this should become a zero-order reaction.

Temperature control in the reaction vessel is an important factor in maintaining a high destruction rate of CCl_4 in the solution. In sonochemistry, it has been reported [7] that one should not attempt reactions in a solvent (here, water) that is near its boiling point (100°C), because the rarefaction cycle causes the water to boil as a result of the reduced pressure generated; consequently, any cavitation bubbles formed will fill with water vapor almost instantaneously. This water vapor could reduce the extremes of temperature and pressure generated and thus decrease the direct destruction efficiency of the organics. On the other hand, the secondary reactions occurring in the liquid phase may be enhanced by operating the system at higher temperatures.

The effect of a steady-state temperature on the destruction efficiency of CCl_4 is shown in Figure 7. About 80% removal efficiency was observed for 4 minutes of irradiation; removal efficiency remained unchanged within a temperature range of $20\text{--}60^\circ\text{C}$. These results illustrate that, with the temperature within this range, increasing the steady-state temperature of the irradiation solutions seems to have little effect on the CCl_4 destruction efficiency. In other words, manipulating the system at the optimum temperature range allows high removal effi-

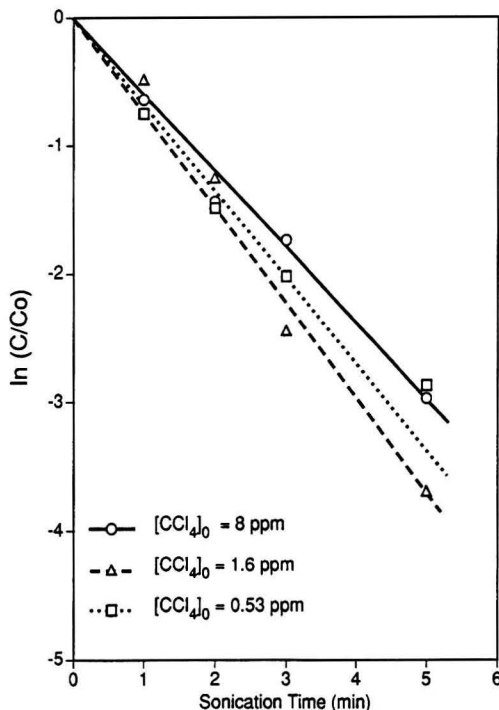


FIGURE 6. First-Order Plot of $\ln[\text{CCl}_4]$ Versus Sonication Time

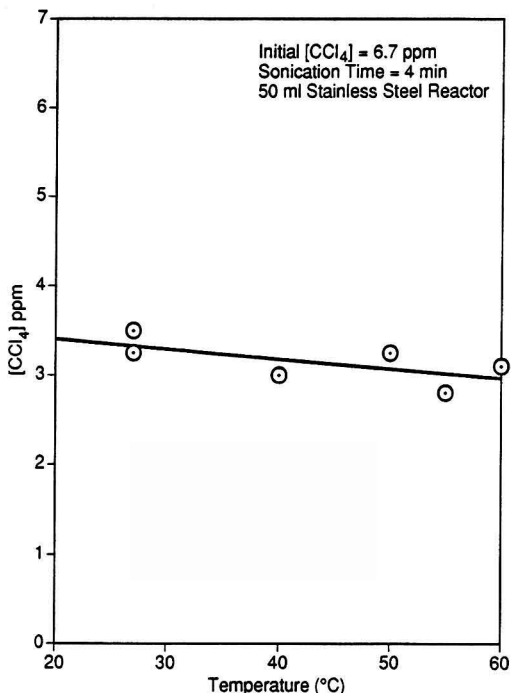


FIGURE 7. Effect of Steady-State Temperature on CCl_4 Sonication

ciencies within reasonable operation times.

Ultrasonic power intensity is also an important factor affecting the CCl_4 destruction rate. In general, any increase in intensity will increase the sonochemical effect [16]. However, it must be realized that intensity cannot be increased indefinitely [17, 18]. With an increase in power intensity, the bubbles

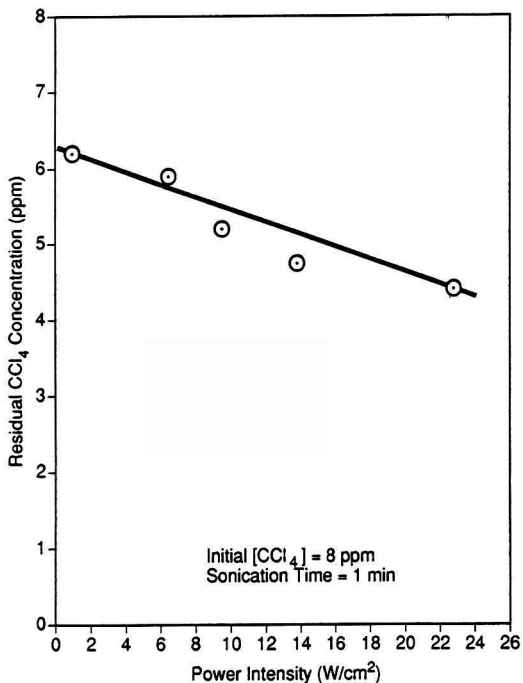


FIGURE 8. Effect of Power Intensity on CCl_4 Sonication

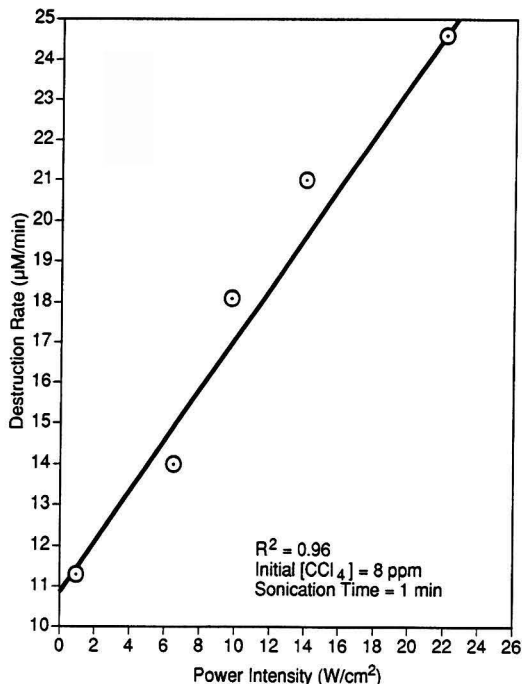


FIGURE 9. Dependence of CCl_4 Destruction Rate on Power Intensity

may grow so large during rarefaction that the time available for their collapse is insufficient; consequently, the effective coupling of the ultrasonic energy to the system is reduced [7].

Figure 8 shows the effect of power intensity upon the destruction of CCl_4 . After 1 minute of irradiation, the residual $[\text{CCl}_4]$ decreases with the increasing power intensity. More CCl_4 molecules are destroyed at higher power intensities. The CCl_4 destruction rate versus power intensity is shown in Figure 9. Within the current experimental range, the destruction rate seems to have a linear relationship to the power intensity. Although threshold intensity was not determined, it is estimated to be lower than the 0.95 W/cm^2 shown in this figure. The destruction rate is negligible if the power delivered into the solution is lower than the threshold intensity.

The relationship between initial pH value and CCl_4 destruction is shown in Figure 10. Residual $[\text{CCl}_4]$ decreases with increasing pH value between pH 3 to pH 9 within the same sonication period. Better sonication efficiency was observed at higher initial pH values; however, such improvement increasingly diminishes as the pH is raised above 6. Since most of the irradiations were conducted at near neutral conditions for groundwater treatment, the initial pH value seems to have a minimal effect upon CCl_4 removal.

Modeling of ultrasonic chemical kinetics was also carried out on the basis of the proposed mechanism described above. If second-order kinetics are assumed, all of the reaction rate constants in the model can be obtained either from published data (reactions 1 to 27 [19-22]) or from experiments (reaction 28). Once determined, these constants are unchangeable and cannot be used as variables. Therefore, no adjustable parameters are included in the model. Reverse reactions were not considered significant because no other chemicals have been added so far and because the concentrations of the products for each reaction were assumed to be much less than those of the reactants.

All of the elementary reactions proposed in the mechanism were transformed into a set of differential equations that de-

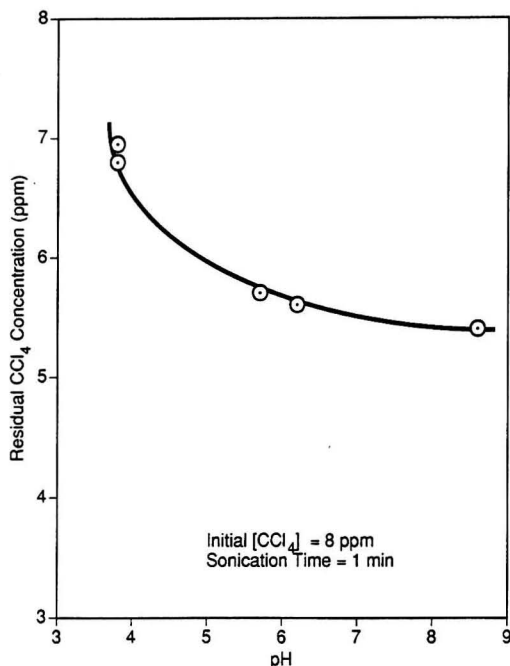


FIGURE 10. Effect of Initial pH Value on CCl_4 Sonication

scribes the time variance of species concentrations on the basis of rate formulas (1) and (2), depending on whether these reactions take place in the bulk-liquid phase or in the cavitation holes. The k_c value in rate formula (2) was obtained by a best fit of the experimental data to the model, which was determined to be 2.5×10^{-11} for the system. With the initial concentration

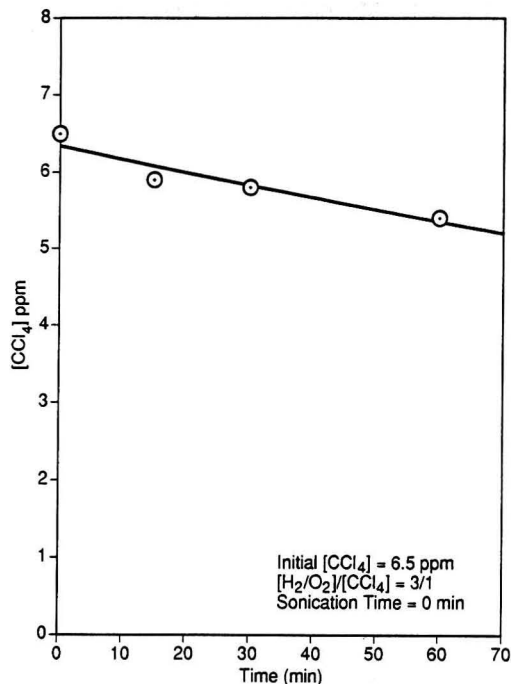


FIGURE 12. Effect of H_2O_2 Dosage on CCl_4 with No Sonication

specified, these equations can be solved readily. Calculated results showed that the model fits the experimental data relatively well at low $[\text{CCl}_4]$ (below 10 ppm). Correlation coefficients greater than 0.99 were obtained. However, deviations were observed at higher $[\text{CCl}_4]$ (46.7 ppm). The predicted destruction rate was greater than that of the experiment. This might be because the organic vapor pressure in the bubble increases with increasing $[\text{CCl}_4]$, and Henry's law no longer applies at this high concentration. In these cases, the activity for each compound in the bubble may need to be taken into consideration.

The sensitivity of each reaction in the model was also tested. Results reveal that the dissolved nitrogen concentration in the system has a minimal effect upon the CCl_4 destruction rate, an effect that is neglected. The major reactions affecting the CCl_4 destruction rate were found to be the dissociation of water molecules and the decomposition of CCl_4 molecules in the cavities. In the bulk-liquid phase, the reaction between OH radicals and CCl_4 was predominant, followed by the reactions of the atomic hydrogen, atomic oxygen, and finally HO_2 radicals.

Hydrogen peroxide (H_2O_2), used as an oxidant, was added to the sample solution to study the effect of oxidant in the ultrasonic field. With sonication, H_2O_2 is known to decompose in the collapsing cavitation bubbles to yield OH radicals. These radicals diffuse into the bulk liquid and increase the radical concentrations in the solution, thus enhancing the destruction rate of organics.

Figure 11 shows the CCl_4 destruction versus H_2O_2 dosages (as $[\text{H}_2\text{O}_2]/[\text{CCl}_4]$ ratio), with 2 minutes of irradiation. Initial amounts of $[\text{CCl}_4]$ as high as 6.5 ppm were reduced to around 0.9 ppm without adding any oxidant and were slowly reduced to about 0.7 ppm as the H_2O_2 dosage increased to 20:1. This decreasing amount is insignificant when compared with the addition of H_2O_2 dosages.

Figure 12 shows CCl_4 destruction versus time with the addition of only H_2O_2 , without ultrasonics. Only slightly de-

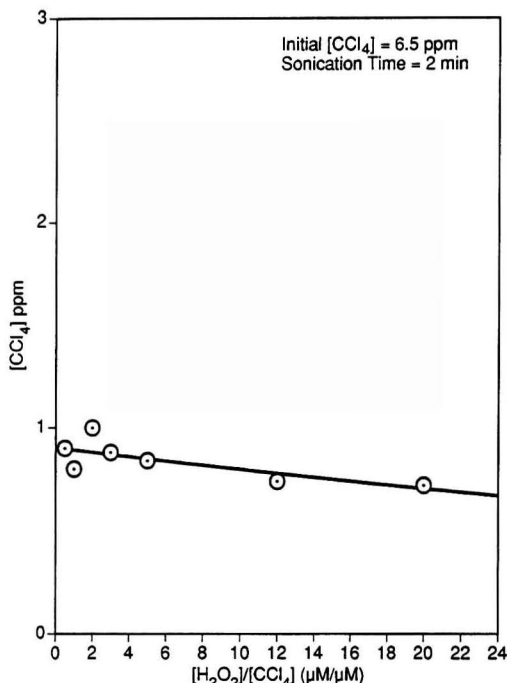


FIGURE 11. Effect of H_2O_2 Dosage on CCl_4 Sonication

creasing amounts of $[CCl_4]$ were observed after 60 minutes reaction time, and the effect was negligible.

These results illustrate that the addition of the H_2O_2 oxidant has almost no effect upon the CCl_4 destruction rate, both with and without ultrasonics. This can be explained by comparing the CCl_4 reaction rate constants between the bulk-liquid phase (less than $10^7 M^{-1} min^{-1}$) and the cavitation hole (around $10^{12} M^{-1} min^{-1}$). The CCl_4 is relatively inactive to radicals because all of the four free electrons are captured by chloride ions and form only single bonds (C-Cl) in the molecule. However, the single bond between C and Cl provides low dissociation energy (only about 80 kcal/mole), thus making it easier for the bonds to cleave in the cavitation holes. Therefore, the bulk-liquid reaction rate constant for CCl_4 is about five orders of magnitude smaller than that in the cavities. This difference makes the reactions in the cavitation holes predominant; therefore, the addition of oxidants has only a minimal effect upon the whole system.

CONCLUSIONS

This study demonstrates that the ultrasonic process is a promising and effective method for the destruction of low concentrations of chlorinated organic compounds such as CCl_4 in water. Removal efficiencies of greater than 99% were achieved through this process. For the treatment of water containing CCl_4 , the major reactions may be the bond-cleavage of water and of CCl_4 in the cavitation hole. Under the current experimental conditions, physical operating conditions, such as steady-state temperature and pH value of the irradiated solution, were found to have little effect upon the CCl_4 destruction rate. However, the CCl_4 destruction rate was found to be significantly affected by the intensity of the ultrasonic energy, with the destruction rate increasing proportionally to the intensity. By contrast, adding hydrogen peroxide as an oxidant had only a negligible effect upon the destruction rate, with or without ultrasonic irradiation.

Finally, mathematical modeling of ultrasonic chemical kinetics via a series of elementary reactions appears to be both a possible and valuable predictive tool for further exploring the means to control the complex ultrasonic process for the detoxification of groundwater.

ACKNOWLEDGMENT

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Remediation of Dichloromethane (DCM) -Contaminated Ground Water

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This case history describes the physical and biological treatment of dichloromethane (DCM)-contaminated ground water following the rupture of an underground pipeline which contaminated an estimated 11,000 m³ (14,000 yd³) of soil and ground water in the early fall of 1983. Air stripping DCM from recovered ground water was initiated and provided an estimated 97% reduction in the ground water concentration of DCM. When it became evident that physical treatment alone would no longer be effective in removing residual DCM from the ground water environment, the practice of air stripping DCM from recovered ground water was terminated. Biological treatment was initiated and provided greater than a 500,000-fold reduction in the ground water concentration of DCM. Biological treatment had far exceeded the ability of physical treatment alone to remediate a ground water environment contaminated with a biodegradable contaminant.

INTRODUCTION

On August 16, 1983, an investigation was undertaken by a client to examine a water main pressure loss at one of its plants. A ruptured water main was discovered in soil saturated with DCM. The DCM had caused deterioration of a polyvinyl chloride (PVC)-constructed water main. The discovery was made that a buried DCM line, located in close proximity to the water main, had ruptured and an undetermined amount of DCM had leaked into the soil and ground water.

An emergency response site investigation was initiated following the discovery of the DCM leak. Interceptor trenches were constructed to contain free-standing product. Free-standing product was collected using vacuum equipment and was staged in vessels for eventual on-site treatment. Trenches were also constructed to determine the extent of lateral migration. Coarse gravel lenses and utility lines in the area permitted DCM to move laterally with little resistance. Monitoring wells were installed. They established that the contamination was within a confining clay layer at the 6-meter (20-ft) level and that the contamination did not reach the drinking water aquifer located at 30 meters (100 ft). The soil type to the 6-meter (20-ft) clay lens varied from sand with some gravel and a little silt to silty sand and silty clay. Monitoring wells were utilized in the perched

aquifer to identify the contaminant plume. Ground water pumping techniques were then employed to contain the spilled DCM.

The emergency response to the spill involved only containment. An investigative phase was then initiated to examine various alternatives for environmentally restoring the site. The spill area was judged to contain 11,000 m³ (14,000 yd³) of DCM-contaminated soil. Following removal of the 120 m³ (160 yd³) of highly contaminated soil to a Class A secure landfill, which represented an estimated 1.1% of the contaminated soil in the spill area, positive placement/suction lift techniques were utilized for recovery and treatment of contaminated ground water.

PHYSICAL TREATMENT

Granular activated carbon adsorption and packed column air stripping were considered for physical treatment of recovered ground water. The selection of a remedial treatment alternative is based upon the volume and concentration of contaminated material to be treated, discharge criteria, total capital investment, and annual operating and maintenance costs. At this site, the anticipated DCM influent concentration

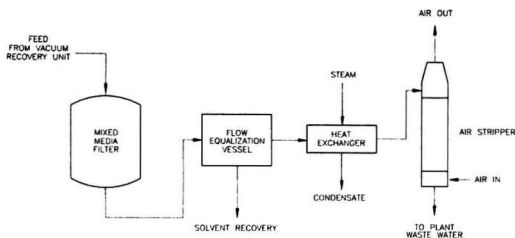


FIGURE 1. Schematic for the physical treatment of DCM-contaminated ground water.

was the deciding factor in the determination of the most appropriate treatment technology.

Based upon a projected influent DCM concentration of 1,000 ppm following phase separation, an estimate was made of the theoretical carbon exhaustion rate to achieve a DCM effluent concentration in the low ppm range. Carbon isotherm data were derived from the USEPA's Treatability Manual [1] and were extrapolated to the higher concentration anticipated. The result was an estimate of 10% for the concentration loading on carbon which was equivalent to the adsorption of 100 mg DCM/g carbon. From previously performed pumping and drawdown tests, the predicted flow rate through the treatment system was 10 to 15 gpm. That prediction yielded a carbon exhaustion rate of 150 lb/day. Furthermore, any slug of DCM to the system would expend the activated carbon at an even faster rate. The additional cost of transporting and disposing of the spent carbon, as well as the additional cost of replacing fresh carbon in the contactor cells, led to the decision not to use granular activated carbon for on-site treatment.

Air stripping was selected as the preferred treatment technology for removal of DCM from the recovered ground water. That decision was based on several important factors. The first factor was the documented ease of stripping DCM from contaminated recovered ground water in past emergency and remedial field operations. Second, the regulatory agencies did not require the implementation of vapor-phase scrubbing units to cleanse air emissions from aeration devices. Third, unlike granular activated carbon, the use of air stripping is generally maintenance-free and regeneration and/or disposal of contaminated media would not be necessary. Finally, several packaged air stripping units were available for immediate dispatch to the site.

To achieve DCM removal efficiencies exceeding 99.9%, the influent wastestream to the air stripper would require heating prior to stripping. Live plant steam was available. Only the addition of a heat exchanger with the necessary controls and instrumentation was required.

Feasibility Evaluation

Characterization and laboratory testing of recovered ground water were performed prior to the final selection of the packed column air stripping treatment alternative [2]. The results of those determinations would define the need for pretreatment prior to air stripping. A particular treatment process may be cost-effective, but the pretreatment costs may render that process cost-prohibitive.

At this site, the treatment system effluent could not exceed 20 ppm for discharge into the plant's wastewater treatment system. The design procedure used to estimate the expected DCM removal efficiency in a packed column air stripper utilizing a nine-foot packing depth has been previously described [2]. With an assumed maximum influent DCM concentration of 16,500 ppm (the estimated solubility at 10°C), the packed

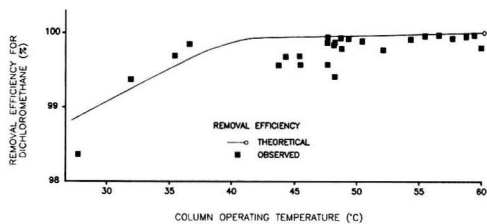


FIGURE 2. Removal efficiency for air stripping DCM from ground water as a function of column operating temperature.

column would be required to achieve a removal efficiency of 99.98% to meet the established discharge criteria of 20 ppm. By fixing liquid and air flow rates and packing height, a predicted column operating temperature of 40°C would be required. In the absence of experimental data to validate the predicted efficiency, the air stripping column was designed for an operating temperature of 40 to 50°C.

Field Implementation

Figure 1 is a schematic of the treatment system designed to treat recovered ground water at a rate of 38 to 57 L/min (10–15 gpm). For removal of sand and other particulates, the ground water was pumped through a downflow mixed-media filter containing anthracite, silica sand, and pea gravel. The media were layered in the filter. The gradation in media pore size from large to small in the direction of flow provided longer filter runs before particulate binding necessitated backwashing of the bed. With backwashing, trapped sediments were recycled back to an influent holding pool.

Ground water leaving the mixed-media filter was piped to a phase separation/clarification/flow equalization vessel. Hydraulic residence time (HRT) in the vessel was fourteen hours. The vessel was a rectangular holding tank that allowed the denser DCM to separate from the water by gravity. Sludge collection equipment removed accumulated solids that escaped the multimedia filter, and float controls in the last chamber maintained a constant flow through the remainder of the treatment system. Liquid from the flow equalization vessel was pumped through a skid-mounted shell-and-tube heat exchanger to raise the water temperature from 10°C to more than 40°C. The heated water was then pumped to the top of the air stripping column for the removal of soluble DCM.

To volatilize DCM in the stripping column, contaminant-free air was passed countercurrent to the wastestream flow. The contaminant-laden air was vented to the atmosphere through a 3.0-meter (10-ft) stack attached to the top of the stripping column. Treatment of the contaminated air with vapor phase carbon was not required. Treated water leaving the stripping column was piped to the plant's wastewater treatment system for further processing. The operation of the treatment system, consisting of mixed-media pressure filtration, phase separation/clarification/flow equalization, and heated volatile air stripping, continued for three months.

The data collected during the operation of the project demonstrated that DCM, as a pure product, settled in the phase separator together with particulate matter that was not trapped by the mixed-media filter. The total volume of pure product collected in that manner did not exceed more than a few liters (gallons). Volatilization of DCM was apparent at the air/water interface in the flow equalization vessel. The DCM concentration entering the air stripping column rarely exceeded 150 ppm. The mixed-media filter removed virtually all particulate matter in the wastestream, and backwashing of the filter was infrequent. The stripping column operating temperature was

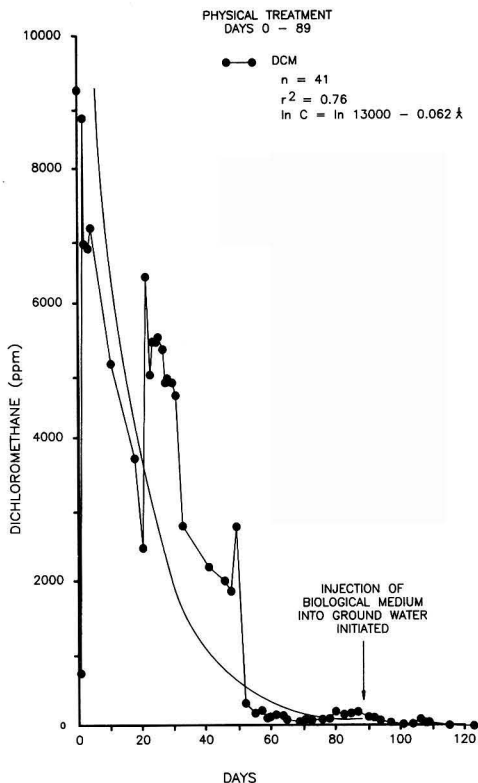


FIGURE 3. Physical removal of DCM in ground water from monitoring well B-5.

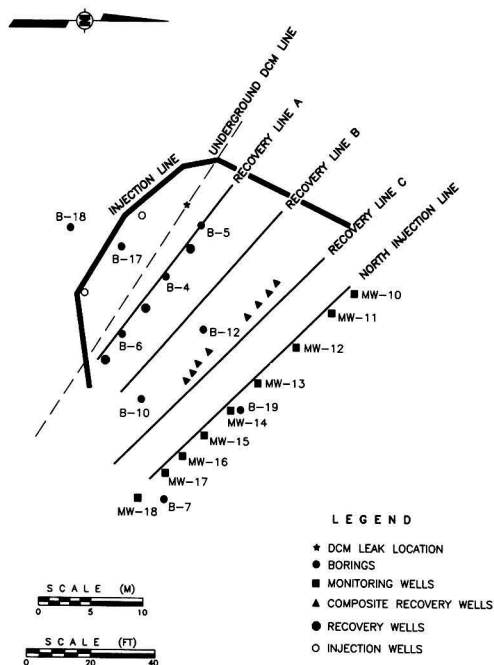


FIGURE 4. Site schematic for August 1983 to July 1987.

maintained between 27 and 60°C. Samples analyzed to evaluate the air stripper efficiency were collected from sample taps located close to the influent and effluent ports of the column. The removal efficiencies actually observed during the three-month operation of the air stripper are presented in Figure 2. The theoretical removal efficiency was calculated from the mass transfer model of Onda and coworkers [3, 4].

First-order kinetics were assumed in calculating the removal rate of DCM from MW B-5 (Figure 3). Monitoring well B-5 was located 6 meters (20 ft) downgradient from the ruptured DCM line (Figure 4). A 50% reduction in the ground water concentration of DCM was observed within the first eleven days of physical treatment. Within two months of field operation, air stripping DCM from recovered ground water resulted in an estimated 97% reduction in the ground water concentration of DCM. By the middle of the third month, it became evident that the effectiveness of physical treatment had appreciably diminished in removing residual DCM from the ground water environment. At the end of the third month, the practice of air stripping DCM from recovered ground water was terminated.

BIOLOGICAL TREATMENT: 1983/1984

Biodegradation of DCM under aerobic conditions in the laboratory was well documented [5-8]. Prior to on-site biological treatment, however, it was necessary to establish the biodegradation potential of DCM in the site matrix.

Feasibility Evaluation

Screening analyses were performed on seventeen selected ground water samples collected from the site on November 17, 1983. These analyses included (1) DCM concentration, (2) aerobic heterotrophic bacterial population density, (3) pH, and

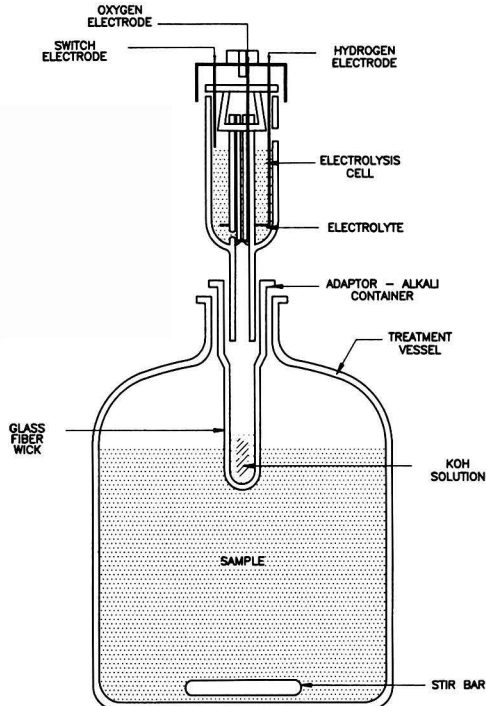


FIGURE 5. Electrolytic respirometer treatment vessel.

(4) available mineral nutrients (i.e., $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-NO}_2\text{-N}$, and $\text{PO}_4\text{-P}$). The analytical results for the screening analyses demonstrated that the DCM-contaminated ground water contained an indigenous bacterial population. The geometric mean (GM) for the seventeen samples analyzed was 2.0×10^4 colony-forming units (CFU)/mL. The GM for the pH of the well samples analyzed was 7.7 which was acceptable for bacterial growth.

The results of the screening analyses also established that $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$ mineral nutrient additions would be necessary for effective biological treatment of the contaminated ground water; $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-NO}_2\text{-N}$, and $\text{PO}_4\text{-P}$ were not detected in any of the ground water samples analyzed. The analytical limits of detection (LODs) for these mineral nutrients were respectively 0.2, 2.0, and 0.06 ppm (Hach Company; Loveland, CO). Nitrogen and phosphorus are essential elements required by bacteria to support enhanced growth on available organics. A deficiency of either of these elements would limit growth on DCM. These elements are generally required in a 100:10:1 ratio of available C:N:P [9]. At a DCM concentration of 300 ppm, a minimum of 4.2 and 0.42 ppm $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$ would respectively be required.

The biodegradation potential of DCM in site matrix ground water was established using the electrolytic respirometer (A.R.F. Products; Raton, NM). DCM loss and chloride release, resulting from the biodegradation of DCM in treatment vessels were used as the test parameters (Figure 5). Chloride concentration was determined using an Orion 96-17B combination chloride electrode with an Orion 901 microprocessor ionanalyzer (Orion Research; Cambridge, MA).

The water sample used for the biodegradation study was collected from an injection pool containing recovered ground water. Sludge collected from one of the plant's industrial wastewater treatment basins was used to inoculate respirometer treatment vessels. The sludge in the basin was reported to have been continuously exposed to low levels of DCM for years and was, therefore, thought to contain populations of bacteria acclimated to DCM.

Table 1 presents the experimental design for the biodegradation study. DCM was added to all treatment vessels to a final concentration of 100 ppm. A concentration of 100 ppm approximated the average DCM concentration found in ground water at the site. Vessels 1 and 2 were replicates which demonstrated the biodegradation potential of DCM. Any non-biological loss of DCM from treatment vessels would be quantified with the abiotic control (that is, vessels 3 and 4). The abiotic control received the microbial poisons KCN and NaN_3 to final concentrations of 320 ppm [10]. Using procedures described by Young and Baumann [11], the respirometer treatment vessels were prepared by adding diammonium phosphate and sodium dihydrogen phosphate to each treatment vessel. Nitrification was not suppressed.

Aliquots (40 mL) were periodically removed from treatment vessels and analyzed for DCM and chloride. DCM loss and chloride release were similar in the biological treatment vessels. The analytical results for one of the biological treatment vessels (vessel 1) are presented in Figure 6. Neither DCM loss nor

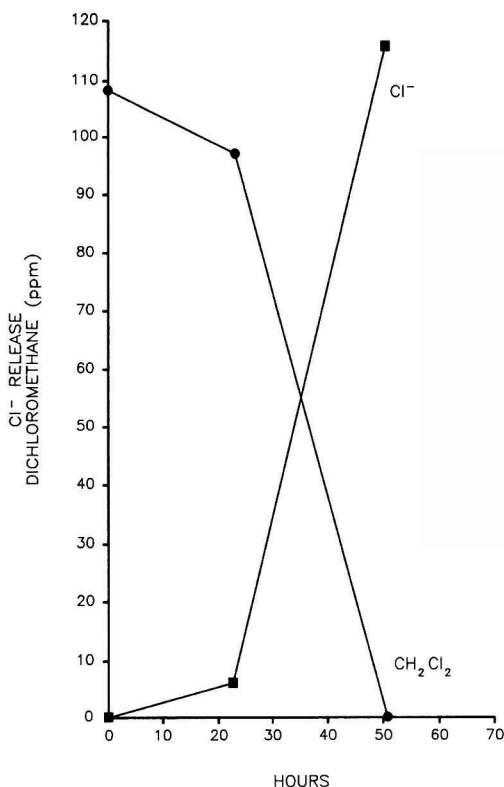
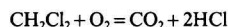


FIGURE 6. Biodegradation of DCM with chloride release in an electrolytic respirometer treatment vessel containing a representative ground water sample.

chloride release was observed in the abiotic control. Bacterial acclimation to DCM occurred within one day. Bacteria from the plant's wastewater treatment system were later used for startup of an aboveground biological reactor for the treatment of recovered ground water prior to reinjection into the DCM-contaminated soil/ground water environment.

Prior to evaluating the biodegradation potential of DCM using a bacterial inoculum from the plant's wastewater treatment basin, bacterial inocula obtained from soil in the vicinity of the ruptured pipeline and from the activated sludge of a domestic wastewater treatment plant were used for the biodegradation study. Within the two week time period the inocula were evaluated, biodegradation of DCM was not observed. With no space available to set up additional respirometer treatment vessels, the decision was made to terminate that attempted acclimation to DCM and to immediately initiate an evaluation of the ability of bacteria from the plant's wastewater treatment basin to biodegrade DCM. The plant's wastewater treatment basin had been receiving low concentrations of DCM for years. With that approach, acclimation to DCM was demonstrated within one day (Figure 6).

The theoretical chloride release for mineralization of DCM was calculated from the following relationship:



For each milligram of DCM mineralized, 0.835 milligrams of chloride would be released. DCM was biodegraded stoichiometrically to chloride in replicate respirometer treatment vessels (Figure 6). Using the following relationship, 130 and 120% of the theoretical chloride release for mineralization of DCM

Table 1 Experimental Design for Treatments in Electrolytic Respirometer Treatment Vessels Used to Establish the Biodegradation Potential of DCM in a Representative Ground Water Sample

Vessel Number	Treatment
1,2	Natural Bacteria Flora Groundwater + DCM + basal salts + sludge inoculum
3,4	Abiotic Control Groundwater + DCM + basal salts + sludge inoculum + poisons

was met in respirometer treatment vessels 1 and 2, respectively:

$$\frac{\text{Actual chloride release}}{\text{Theoretical chloride release}} \times 100$$

Analytical results from the biofeasibility evaluation indicated that the DCM was completely oxidized to carbon dioxide with chloride release. The lack of an appreciable lag period indicated that naturally occurring bacteria from the plant's wastewater treatment basin were adapted to DCM.

Field Implementation

A ground water recovery and treatment system, similar to that described for other biological remediation projects [12], was put into immediate operation. The injection/recovery wells used for the air stripping operation were now utilized for biological treatment. Air stripping of DCM from recovered ground water was replaced with biological treatment utilizing a suspended growth system for aboveground treatment.

In addition to providing efficient biological treatment, this system permitted wasting of adapted bacteria into the contaminated soil/ground water environment. The injection system was used to introduce adapted bacteria into that environment and to provide the chemical environment necessary to support enhanced bacterial growth. The recovery system was used to withdraw DCM-contaminated ground water for aboveground treatment. Effluent from the treatment system was then re-injected into the subsurface environment. Biodegradation of DCM took place in the soil/ground water environment as well as aboveground in the biological treatment system.

On day 82, batch treatment of DCM-contaminated ground water was initiated. To maintain a DCM-adapted bacterial population, air containing DCM vapor was bubbled into the bioreactor. Between days 82 and 87, an 80% increase in chloride concentration in the bioreactor was observed as a result of chloride release from the biodegradation of DCM (Figure 7). Between days 87 and 90, the contents of the bioreactor were drained into an injection pool and then the bioreactor was refilled. Injection of DCM-adapted bacteria into the soil/ground water environment began on day 89.

Batch treatment of DCM-contaminated ground water was again performed in the bioreactor between days 90 and 92. A 110% increase in chloride concentration was observed as a result of DCM biodegradation. The bioreactor was again drained into the injection pool and then refilled. On day 95, continuous biological treatment was initiated. Over the ten-day operational phase of continuous biological treatment, the effluent chloride concentration averaged $131 \pm 65\%$ ($\bar{x} \pm s$, $n = 9$) greater than the influent concentration.

The removal of DCM from the ground water environment was rapid. In MW B-5 (Figure 8), a downgradient well located 6 meters (20 ft) from the DCM spill, a 50% reduction in DCM concentration was observed within eight days of biological treatment. The rate of decrease was assumed to be first-order [13]. With the onset of winter, biological treatment at the site was temporarily suspended. Winterization of the treatment system would have been required for continuation of active biological treatment.

At that time, a 97% reduction in DCM concentration was observed since the biological treatment was initiated. Theoretical chloride release for biodegradation of 186 ppm of DCM (that is, from 192 to 6 ppm DCM) is 155 ppm. The observed chloride release was 156 ppm; i.e., the chloride concentration in MW B-5 increased from 175 ppm on day 80 to 331 ppm on day 123. Biological treatment, therefore, was considered responsible for the removal of DCM from that ground water environment.

Active biological treatment was suspended on January 2, 1984, and did not resume until August 1987, when the residual

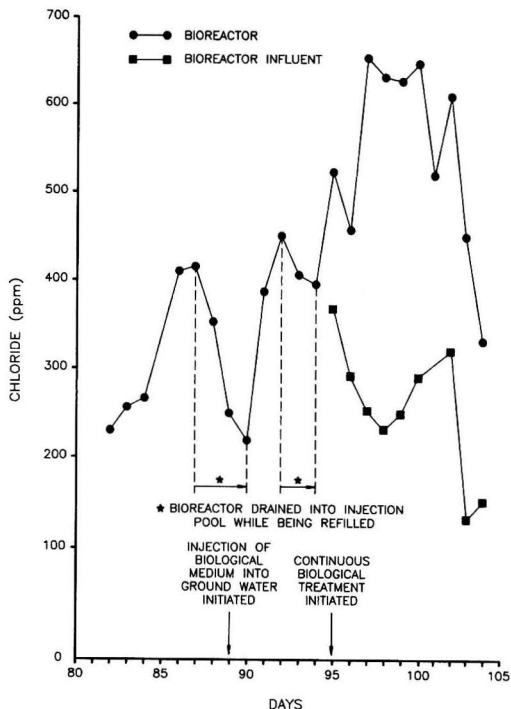


FIGURE 7. Chloride release in the bioreactor resulting from biodegradation of DCM.

DCM contamination remaining in the soil and ground water was addressed by the resumption of full-scale on-site biological treatment.

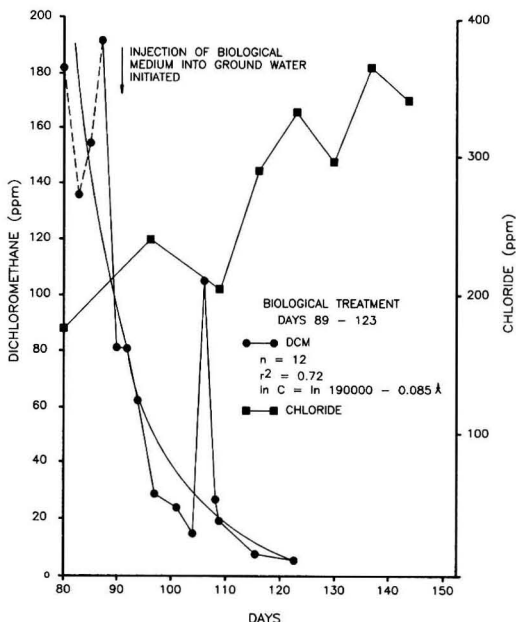


FIGURE 8. Biological removal of DCM in ground water from monitoring well B-5 as a function of time.

Table 2 Analytical Results of Screening Analyses Performed on DCM-Contaminated Ground Water Samples Collected from the Site in August 1985 and Used to Establish the Biodegradation Potential of DCM by the Indigenous Microflora

Location	DCM (ppm)	Chloride (ppm)	NH ₃ -N (ppm)	PO ₄ -P (ppm)	pH	Aerobic Heterotrophic Bacteria (CFU/mL)
B-4	90	510	0.84	<0.06	9.7	3.1 × 10 ⁵
B-5	9.5	200	32	<0.06	8.6	8.0 × 10 ⁶
B-6	14,000	490	3.9	<0.06	7.2	5.4 × 10 ²
B-17	73	450	4.5	<0.06	6.6	1.4 × 10 ²
WWTB ¹	20	990	2.2	<0.29	8.6	3.1 × 10 ⁶

¹Wastewater Treatment Basin

BIOLOGICAL TREATMENT: 1987/1988

Feasibility Evaluation

Prior to renewal of full-scale treatment, a biofeasibility study was performed in August 1985 to determine the potential of the indigenous microflora in the DCM-contaminated soil/ground water environment to biodegrade DCM. Ground water samples from MWs B-4, B-5, B-6, and B-17 and water from the plant's wastewater treatment basin were used for the study (Figure 4). Screening analyses were performed on those samples. The results of those analyses are presented in Table 2.

Analytical results of the screening analyses indicated that, with the exception of ground water from MW B-6, the environments tested did not appear toxic to bacterial growth. The bacterial plate count for B-6 was 5.4×10^2 CFU/ml. The DCM concentration in B-6 was 14,000 ppm. The plate counts for the remaining locations ranged from 3.1×10^2 to 8.0×10^6 CFU/ml. The DCM concentration in those locations ranged from 9.5 to 90 ppm. The high DCM concentration may have been responsible for the lower bacterial population density observed in B-6.

The analytical results of the screening analyses also indicated that mineral nutrient addition and/or pH adjustment would be required for enhanced biological treatment. Orthophosphate-phosphorus was not detected in any of the ground water samples analyzed. Only 50% of the ground water samples analyzed were within a pH range generally considered acceptable for enhanced bacterial growth.

The biodegradation potential of DCM in the collected samples was evaluated using the electrolytic respirometer (Figure 5). For the study, mineral nutrient concentrations and pH were maintained within acceptable ranges for enhanced bacterial growth. DCM loss and chloride release in treatment vessels were used as the test parameters.

A two-phase study was performed. DCM-basal salts-yeast extract (5 ppm) medium [10], inoculated with washed (0.02 M phosphate buffer, pH 7.2) cell suspensions from each of the samples collected, was used for Phase 1. The objective of this phase of the study was to evaluate the potential of the indigenous microflora to biodegrade DCM. Adapted microorganisms from Phase 1 were used in Phase 2 as inocula to evaluate the biodegradation potential of DCM in the site matrix samples. Abiotic controls were prepared for the Phase 1 and Phase 2 studies to quantify nonbiological loss of DCM from treatment vessels.

Throughout the Phase 1 study, the environment remained favorable for bacterial growth (Table 3). Biodegradation of DCM was demonstrated in treatment vessels containing inocula from B-5, B-6, B-17, and the wastewater treatment basin after sixteen, twenty, seven, and twenty days, respectively. Biodegradation of DCM in a treatment vessel inoculated with a cell suspension from B-4 was not demonstrated after thirty-four days.

The biodegradation potential of DCM in site matrix samples was similarly determined in the Phase 2 study. Washed cell suspensions from Phase 1 treatment vessels were added to the treatment vessels containing the site matrix samples. Ground water from B-6 was diluted with laboratory-grade water to 10% (vol/vol) full strength since the high DCM concentration in the site matrix sample was suspected to be the cause of the low bacterial population density observed in ground water at that location. Biodegradation of DCM was demonstrated within seven days in all site matrix samples analyzed.

Based on the results of the feasibility evaluation, the conclusion was made that the indigenous microflora may be utilized for remediation of the DCM-contaminated ground water matrices analyzed. For enhanced biological treatment, oxygen and mineral nutrient addition and pH adjustment would be required.

Table 3 DCM, Chloride, NH₃-N, and PO₄-P Concentrations, pH, and Aerobic Heterotrophic Bacterial Population Density in Electrolytic Respirometer Treatment Vessels for the Phase 1 Study

Inoculum	DCM (ppm)		Chloride (ppm)		NH ₃ -N (ppm)		PO ₄ -P (ppm)		pH		Aerobic Heterotrophic Bacteria (CFU/mL)	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
B-4	130	81	1.6	1.6	180	200	470	450	7.5	7.5	1.2 × 10 ⁴	5.9 × 10 ⁴
B-5	160	<1.0	1.9	170	220	180	520	440	7.0	6.3	1.9 × 10 ⁵	1.7 × 10 ⁷
B-6	210	<1.0	2.2	170	190	200	490	400	7.5	6.8	4.6 × 10 ¹	2.0 × 10 ⁶
B-17	140	<1.0	2.4	200	190	180	480	420	7.1	6.3	8.7 × 10 ²	1.1 × 10 ⁷
WWTB ¹	200	<1.0	2.7	170	190	200	490	430	7.5	7.0	4.2 × 10 ⁴	4.2 × 10 ⁶
B-4 ²	210	99	500	500	170	200	490	430	8.3	8.4	<1.0 × 10 ¹	<1.0 × 10 ¹

¹Wastewater Treatment Basin

²Abiotic Control

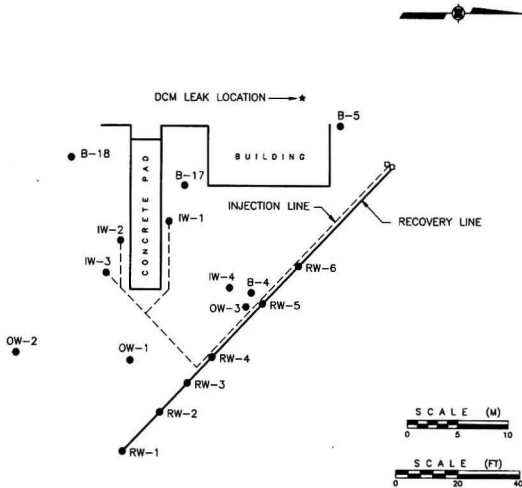


FIGURE 9. Site schematic for the 1987/1988 field operation.

Field Implementation

Prior to initiating the field operation, the analytical data from monthly analyses of ground water samples collected between June and December 1986 from wells B-4 through B-7, B-10, B-12, B-17 through B-20, MW-10 through MW-17, and recovery well RW-11 (Figure 4) were reviewed. Those samples were analyzed for DCM, chloride, and pH.

Based on the results of those analyses, a ground water injection/recovery system was installed in July 1987. The system focused on remediating the area enclosed by MWs B-4, B-6, B-12, and B-17. The DCM concentration in those wells in 1986 approximated 4,000, 10,000, 300, and 1,000 ppm, respectively. The size of the area requiring remediation was seven times smaller than that addressed in 1983. To effectively apply remediation within that area, additional observation wells (that is, OW-1 through OW-3), injection wells (that is, IW-1 through IW-4), and recovery wells (that is, RW-1 through RW-6) were installed (Figure 9).

A vacuum recovery unit was utilized for the recovery of DCM-contaminated ground water. From the vacuum recovery unit, ground water was pumped to a flow equalization chamber which was also used for nutrient addition, pH adjustment, and aeration. The treated water was then reinjected into the soil/ground water environment for enhanced *in situ* biological treatment. The flow through the aboveground system ranged from 7.5 to 15 L/min (2-4 gpm).

The DCM concentrations in monitoring wells at the initiation of the field operation in August 1987 and after eight months

Table 4 DCM Concentration in Monitoring Wells at the Initiation of Field Operation in August 1987 and After Eight Months of Enhanced Biological Treatment

Monitoring Well	DCM Concentration (ppm)	
	August 1987	April 1988
OW-1	11	<0.005
OW-2	<2	<0.005
OW-3	5,200	130
B-4	3,200	0.35
B-5	<2	<0.005
B-17	1,500	<0.005
B-18	<2	<0.005

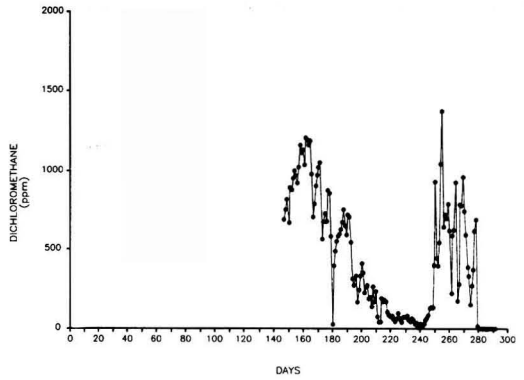


FIGURE 10. DCM concentration as a function of time in observation well OW-3 from August 5, 1987 to May 24, 1988 (day 295).

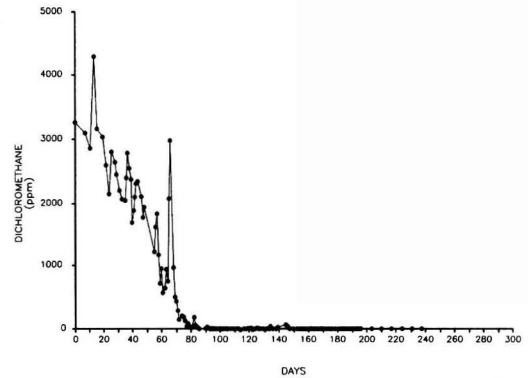


FIGURE 11. DCM concentration as a function of time in monitoring well B-4 from August 5, 1987 to March 30, 1988 (day 238).

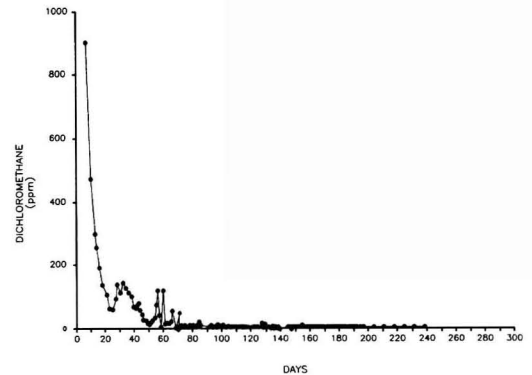


FIGURE 12. DCM concentration as a function of time in monitoring well B-17 from August 5, 1987 to March 30, 1988 (day 238).

of field operation are presented in Table 4. Figures 10 through 12 present the DCM concentration in OW-3, MW B-4, and MW B-17 as a function of time beginning on August 5, 1987. The spikes of DCM observed in these wells are attributed to the flushing of pockets of DCM within the unsaturated zone (that is, vadose zone) into ground water by the injection system. Within eight months, the DCM concentration in the monitoring wells was reduced as much as 300,000 fold. Active biological treatment was suspended on May 24, 1988, when DCM was reduced to less than 2 ppm in all monitoring wells at the site. By June 1, 1988, DCM was reduced to less than 10 ppb in all monitoring wells at the site with the exception of MW B-4 [14]. Currently, the DCM concentration in MW B-4 ranges between 0.05 and 0.5 ppm. The state regulatory agency will consider the project completed when DCM remains less than 10 ppb in MW B-4 over a three-month period based on monthly analysis of ground water from that well.

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Effect of Chemical Pretreatment on Anaerobic Biodegradation of Refractory Organic Compounds

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The potential for using chemical oxidation to enhance anaerobic biodegradability and reduce toxicity of two model phenolic compounds (o-cresol and 2,4-DNP) was evaluated. Batch bioassays were performed on the model compounds and their oxidation samples to determine biodegradability and toxicity in batch methanogenic cultures. Ozone, hydrogen peroxide, and potassium permanganate were the three oxidants examined in this study. A dose of approximately 5 moles hydrogen peroxide, in the presence of a ferrous iron catalyst (Fenton's reagent), 7 moles permanganate, or 25 moles of ozone per mole of o-cresol was needed to significantly enhance anaerobic biodegradability of oxidation samples. Approximately 2.5–4.5 moles of hydrogen peroxide or 7 moles of ozone per mole of 2,4-DNP reduced methanogenic toxicity by 50%.

INTRODUCTION

Phenolic compounds represent the major constituents present in a wide spectrum of industrial wastewaters such as coal conversion, coke preparation, petroleum refineries, pulp and paper, and photoprocessing [1]. Many of these compounds can cause adverse effects on human health and receiving waters if discharged without proper treatment. Effective treatment of these materials has been demonstrated by chemical oxidation using oxidants such as ozone [2–7], hydrogen peroxide [8, 9], and permanganate [10]. Reaction mechanisms of phenols with these oxidants have been proposed by several researchers. Permanganate oxidation in acid and neutral solutions may be accomplished by permanganate ions and several ions derived from the tri- and tetravalent states of manganese [11]. In basic solutions, the oxidation of phenols may be initiated by transfer of an electron from the phenolate ion to permanganate to form phenoxy free radicals. The phenoxy free radicals so formed are then involved in coupling and oxidation reactions resulting in formation of o- and p-diphenoquinones as the intermediates [10]. The strong oxidation power of hydrogen peroxide, however, is attributed to the formation of hydroxyl free radicals

in the presence of a ferrous iron salt [8]. The oxidation of phenol by this reagent may produce catechol and hydroquinone which are further oxidized to muconic acid and the corresponding quinones [8]. The oxidation of phenol by molecular ozone, on the other hand, probably involves the electrophilic attack by ozone of the ortho, para-directive phenol molecular and 1,3 dipolar cyclo addition of ozone [12]. The electrophilic attack yields catechol and hydroquinone as the major intermediates while the dipolar cyclo addition causes direct ring cleavage to produce muconic acid or muconaldehyde. Ozonation of substituted phenols may involve oxidation of substituents groups. The methyl group of o-cresol may be oxidized to carboxylic acid upon initial ozonation and produce salicylic acid as the early ozonation intermediate. At pH above 8, ozone is unstable and tends to react with HOH to form highly reactive hydroxyl radicals which attack more rapidly and indiscriminately than ozone. Consequently, reaction mechanisms and intermediates formed during oxidation may differ depending on the media pH.

Chemical oxidation to achieve complete reduction in chemical oxygen demand (COD) or total organic carbon (TOC), however, would be exceedingly costly and time consuming. Although biological oxidation may be the most cost-effective

treatment method for high-strength wastewaters, its effectiveness is generally limited to nontoxic and biodegradable wastes. Chemical oxidation pretreatment of wastewaters containing biorefractory or toxic compounds followed by biological processes seems to be a logical approach to treat this type of waste.

Anaerobic biological treatment offers the advantages of no oxygen requirement, low waste biomass production, and the generation of methane gas. However, very little attention has been paid to assess the potential for using chemical oxidation to enhance anaerobic biological treatment of biorefractory or toxic materials. In this study, anaerobic bioassay of two model phenolic compounds and their chemical oxidation samples was performed to determine the effect of chemical oxidation on their biodegradability and toxicity.

MATERIALS AND METHODS

Phenolic Compounds

o-Cresol and 2,4-dinitrophenol (DNP) were the model compounds studied. These compounds were selected because previous work has shown that they are biorefractory and/or inhibitory to methanogenic cultures [13, 14]. All phenolic solutions were prepared by adding a predetermined amount of phenolic compounds to a proper volume of distilled and deionized water.

Chemical Oxidation Pretreatment

Ozone was generated from pure oxygen using a Welsbach Model T-816 Ozonator. Ozonation of model compounds was conducted in a 500 mL gas-washing bottle (6 cm OD × 24 cm) fitted with a ground glass joint. A coarse sintered glass dispersion tube delivered ozone to the bottom of the reactor at an average rate of 0.23 mmol/min. During ozonation, the reactor content was stirred vigorously with a magnetic stirrer to maintain good mixing. The reaction of phenols with hydrogen peroxide or permanganate was conducted in 500 mL batch stirred reactors. Ozonation and permanganate oxidation were conducted with both unbuffered and buffered solutions. The buffered solutions were prepared by adding 0.02 M boric acid and 0.02 M sodium borate and adjusting pH to 9 with NaOH. Ferrous iron (FeCl₂) was added as a catalyst for hydrogen peroxide oxidation at an optimum concentration ratio of phenolic compounds to iron of 100 to 1 and the reaction pH values were within the optimum range of 3–4 [8, 9, 15]. The reactors were covered by aluminum foil during the course of oxidation and samples were immediately stored in dark bottles and refrigerated prior to analysis. Oxidant doses were expressed as mole oxidant/mole compound initially present.

Methanogenic Culture

A phenol-enriched methanogenic culture was used as the seed inoculum for all biodegradability and toxicity tests. This culture had been developed for more than 3 years from seeds obtained from the Department of Civil Engineering, University of Illinois (courtesy of Dr. Makram T. Suidan) and digested municipal wastewater sludge (West Hickman Treatment Plant, Lexington, Kentucky) using a 14-L, continuous flow fermentor (Model MF-114, New Brunswick Scientific Co., Edison, NJ). The feed solution contained 4000 mg/L phenol as the primary substrate and 5 mg/L each of other organic compounds (o-cresol, m-cresol, p-cresol, 2-ethylphenol, 3-ethylphenol, 4-ethylphenol, catechol, resorcinol, hydroquinone, salicylic acid, m-hydroxybenzoic acid, and p-hydroxybenzoic acid) along with a salt and vitamin solution. The fermentor was operated at 35°C and 30-day liquid detention time with pH maintained at 7 using sodium bicarbonate. Table 1 summarizes the performance of the fermentor throughout this study.

Table 1 Summary of Performance of the Methanogenic Fermentor

	Average	Range
Total gas production, mL/day	1820	1460–2190
Gas composition, %		
methane	63.6	61.9–66.5
carbon dioxide	35.4	31.5–37.1
Volatile suspended solids, mg/L	260	164–396
Phenol and other feed compounds, mg/L	BDL*	BDL

*below detention limit (≤ 1 mg/L)

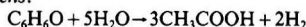
Batch Bioassay

Two batch test procedures, the biochemical methane potential (BMP) and the anaerobic toxicity assay (ATA), were used to evaluate the anaerobic biodegradability and toxicity of oxidant treated samples, respectively. The procedures were a modification of Owen et al. [16] and involved the placement in a 125-mL serum bottle of 50 mL sample and 50 mL methanogenic culture while under the purge of an oxygen-free 30% CO₂ and 70% N₂ gas mixture. Sodium sulfide (500 mg/L) and L-cystine hydrochloride (500 mg/L) were added to provide a reducing environment.

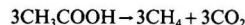
Before being transferred to serum bottles, oxidation samples were prepared by removing excess oxidants. Dissolved oxygen and residual ozone were removed by purging the samples with nitrogen gas for 15 min. Any excess hydrogen peroxide was removed by reacting with added ferrous iron [17]. Residual permanganate was removed by first acidifying the samples to form MnO₂ ($4 \text{MnO}_4^- + 4\text{H}^+ = 3\text{O}_2 + 2\text{H}_2\text{O} + 4\text{MnO}_{2(s)}$). The solid MnO₂ so formed was then removed from solutions by filtering the samples through a 0.45 μm membrane filter.

To evaluate toxicity to the specific bacterial groups in the mixed methanogenic culture, two types of substrates (acetic acid and phenol) were used in the ATA tests. Acetic acid was used to assess sample toxicity toward methanogenic bacteria while phenol was selected to estimate toxicity toward acetogenic bacteria in the phenol-enriched mixed culture. Acetic acid or phenol was used as the test substrate to allow for an independent evaluation of toxicity toward the specific bacterial groups in the methanogenic cultures. A consortium of acetogenic and methanogenic bacteria is responsible for the degradation of phenol to methane while conversion of acetate to methane is achieved by the methanogens alone [18, 19]. Three distinct bacterial morphotypes were also observed in the phenol-enriched methanogenic culture used in this study. The following steps in the overall conversion of phenol to methane were proposed before [20]:

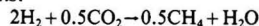
Phenol-degrading acetogens:



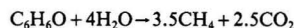
Acetate-utilizing methanogens:



Hydrogen-utilizing methanogens:



Sum:



Based on the above stoichiometrical relationship, acetate is the major precursor of methane and it accounts for approximately 86% of methane produced during anaerobic degradation of phenol. Therefore, using phenol and acetate as test substrates may provide information on which bacterial group is more susceptible to inhibition caused by oxidant treated samples.

All samples were buffered at pH 7.0 with sodium bicarbonate

before finally sealed with butyl rubber stoppers and placed on a continuous shaker in a 35°C constant temperature room. Duplicates were run for all samples, including the controls which contained no chemical oxidation samples.

ANALYTICAL PROCEDURE

Gas samples were withdrawn from the test bottles with syringes at proper intervals for the determination of methane content in the BMP and ATA tests. Gas production was monitored by displacement of the plunger in an appropriate sized wetted glass syringe. Gas composition was determined with a gas partitioner (Fisher Model 1200) using certified calibration standards. Chemical oxidant treated samples were analyzed for COD, TOC, initial compound, and organic acids. COD was determined by using Method 508 of *Standard Methods* [21]. TOC was measured by chemical ultraviolet oxidation and infrared detection using a carbon analyzer (Dohrman Model DC-80). o-Cresol, 2,4-DNP, and salicylic acid were analyzed by a liquid chromatograph (Varian Model 5020) equipped with a variable wavelength UV detector and a MicroPak MCH-5 C₁₈ reverse phase column at ambient temperature. Detection wavelength was set between 270 and 310 nm corresponding to the absorbance maximum of the compound. All organic acids except glyoxylic acid and salicylic acid were analyzed by a modified procedure of Salanitro and Muirhead [22] in which the samples were subjected to a butyl-esterification process. BF₃-Butanol was used as the butylating agent, and the dry salts of the acids were heated at 60°C for 20 min in a temperature bath. The butyl esters were then analyzed by a gas chromatograph (Varian Model 3400) with a 50 m × 25 mm SPB-1 fused silica capillary column and a FID detector. The carrier gas was helium, and a split ratio of 90:1 was used. Oven temperature was increased from 50°C to 170°C at 12°C/min, then 20°C/min to 230°C. The detector and the injector temperature were both set at 250°C. Glyoxylic acid was analyzed by measuring spectrometrically the ionized species of glyoxylic dinitrophenylhydrazine at 513 nm [4].

BIODEGRADATION AND TOXICITY PARAMETERS

Biodegradability of reaction samples was indicated by the ratio of the net and the potential methane production. The net methane production was determined by subtracting methane produced in the seed-blank bottles from that measured in test

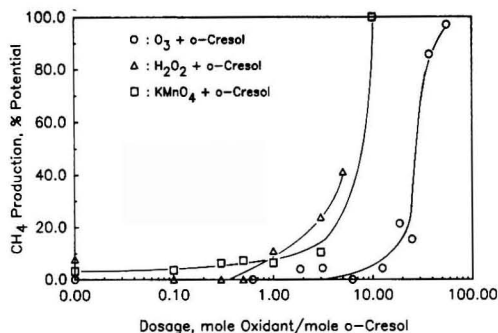


FIGURE 1. Anaerobic biodegradability of oxidant treated o-cresol

bottles after incubation for at least 30 days. Experimental errors of determining methane production were estimated to be within ±10%. The methane data were corrected for moisture content and converted to 0°C and 1 atm. The methane content of the liquid as determined from Henry's law and the partial pressure of the methane in the gas phase was also included in the data. The methane potential was calculated based on the measured COD of the sample and a conversion factor of 0.35 CH₄/g COD at 0°C and 1 atm [23]. Inhibition to the acetate-utilizing methanogens was indicated by a decreased rate of methane production relative to the acetate control while inhibition with phenol degradation was indicated by a decreased rate of methane production relative to the phenol control.

RESULTS AND DISCUSSION

BMP Tests

Figure 1 demonstrates the anaerobic biodegradability of oxidant pretreated samples of unbuffered 200 mg/L o-cresol under a range of the three oxidant doses. Figure 1 shows that net methane production from the untreated o-cresol (control, at 0 mole oxidant/mole o-cresol) was less than 8% of its potential, indicating that o-cresol was not significantly degraded. However, the biodegradability of the treated o-cresol increases with increasing dose of oxidants. Although o-cresol might be degraded at a very low level as the o-cresol concentration in the effluent from the methanogenic fermentor was less than 1 mg/l, 200 mg/l o-cresol was used in the BMP tests to assess

Table 2 Summary of Chemical Oxidation Pretreatment of o-Cresol

o-Cresol concentration (initial, mg/l)	Oxidant and dose (mole/mole o-Cresol)	End pH at highest dose	Oxidant needed for 100% removal (mole/mole o-cresol)	Product identified
200	O ₃ : 0.6-55.9	2.7	6.1	Formic, acetic,
600	O ₃ : 0.6-49.6	2.5	5.0	propionic, glyoxylic,
600	O ₃ : 0.6-49.6	8.3	4.1	oxalic and salicylic acid
200	H ₂ O ₂ : 0.1-10	3.1	4.0	Formic, acetic, and oxalic acid
600	H ₂ O ₂ : 0.1-10	2.8	5.0	
200	KMnO ₄ : 0.1-10	3.3	3.0	—
600	KMnO ₄ : 0.1-10	4.7	—	

Table 3 Summary of Chemical Oxidation Pretreatment of 2,4-DNP

2,4-DNP concentration (initial, mg/l)	Oxidant and dose (mole/mole 2,4-DNP)	End pH at highest dose	Oxidant needed for 100% removal (mole/mole 2,4-DNP)	Product identified
100	O ₃ : 10.6-190.4	2.8	21.1	Formic, acetic, glyoxylic, and oxalic
100	O ₃ : 10.6-190.4	8.3	14.9	—
100	H ₂ O ₂ : 0.1-5	2.8	5.0	—
100	KMnO ₄ : 0.1-10	2.7	> 5.0	—
100	KMnO ₄ : 0.1-10	8.7	3.0	—

the effect of chemical oxidation on a moderate strength wastewater.

The data in Figure 1 indicated that the observed increase in biodegradability of treated samples was faster with hydrogen peroxide or permanganate than with ozone based on oxidant doses. For example, for 1 mole of o-cresol, about 5 moles hydrogen peroxide (highest dose applied) or approximately 7 moles permanganate were needed to obtain 40% biodegradable products while approximately 25 moles ozone were needed to achieve the same biodegradability. The ozone dose far exceeded the observed requirement of 6.1 moles/mole for complete removal of nonbiodegradable 200 mg/L o-cresol by oxidation (Table 2), indicating slow formation of biodegradable products during ozonation. The data in Table 2 and Figure 1 also suggested that complete or near complete oxidation of o-cresol was needed to obtain significant methane production from the o-cresol carbon. In the case of 2,4-DNP, chemical oxidation (see Table 3) was ineffective to enhance biodegradability. All three oxidant treated samples were not degraded as no significant net methane production was noted in any of these sample bottles.

Several organic acids were identified as the oxidation products during the reaction with ozone and peroxide oxidation. An example of organic acids formation is shown in Figure 2 with ozone as the oxidant. Identified organic acids are summarized in Tables 2 and 3. These acids accounted for 21-85% and 18-33% TOC present after complete removal of o-cresol by ozonation and peroxide oxidation, respectively. For 2,4-DNP, organic acids identified accounted for 42-77% TOC after the disappearance of the initial compound during ozonation. Salicylic acid was detected during ozonation of o-cresol under relatively lower doses of ozone (≤ 3 moles/mole) but its level was never higher than 1 mg/L. Although permanganate treated samples were not analyzed for organic acids, formation

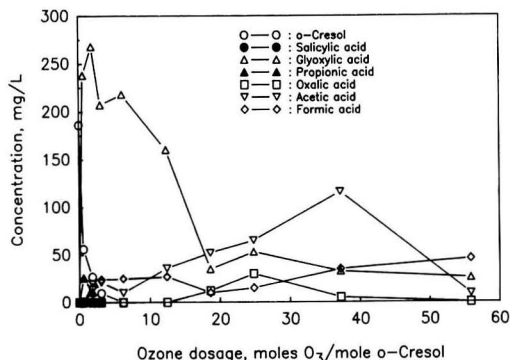


FIGURE 2. Organic acids formation during ozonation of o-cresol (unbuffered)

of these acids was suggested by a rapid drop in pH during the reaction as were the cases with ozone and peroxide in unbuffered solutions. The anaerobic biodegradability of these identified acids (except the negligible salicylic acid) was examined by the BMP tests and results indicated that formic acid, acetic acid, and propionic acid were biodegradable to methane while oxalic acid and glyoxylic acid were not significantly degraded in the phenol-enriched methanogenic culture. During ozonation of 200 mg/l o-cresol, the nonbiodegradable glyoxylic acid and oxalic acids accounted for only 5.4% of the measured TOC while the biodegradable acetic acid, formic acid, and propionic acid constituted 15.2% of the measured TOC under an ozone dose of 55.9 moles/mole o-cresol. Therefore, the near complete conversion to methane from ozone treated 200 mg/l o-cresol at the highest doses as observed in Figure 1 may be largely due to formation of other unidentified, biodegradable products. However, the observation that no net methane was produced in any of the bottles containing treated, 2,4-DNP suggested that biodegradation of biodegradable organic acids was inhibited by oxidation reaction products in the treated samples.

ATA Tests

In order to evaluate the inhibitory nature of the treated samples, the ATA tests were conducted using phenol and acetate as the test substrates, respectively. Figures 3 and 4 show the cumulative methane production in sample as well as control bottles with 600 mg/L o-cresol as the initial compound and permanganate as the oxidant. Figure 3 was obtained with acetic acid as the test substrate while the data in Figure 4 were collected with phenol as the test substrate. The controls were

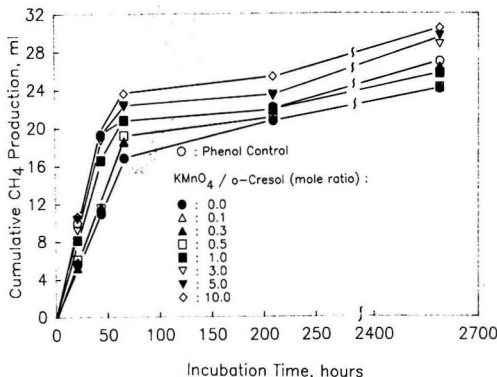


FIGURE 3. Methane production from added acetic acid in permanganate oxidation products

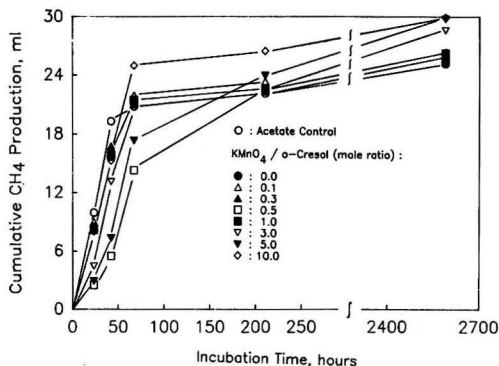


FIGURE 4. Methane production from added phenol in permanganate oxidation

spiked with a test substrate only and received no samples (either treated or untreated). The acetate control received only 500 mg/L acetate, whereas the phenol control received only 200 mg/L phenol.

The data in Figure 3 indicate that both the untreated o-cresol and all of the permanganate treated o-cresol were slightly inhibitory to the acetate-utilizing methanogens during the initial 44 hours of incubation. The untreated o-cresol and o-cresol treated with doses of 1 mole permanganate/mole or less also exhibited inhibition to the phenol degraders during the first 44 hours of incubation as the rates of methane production were lower than those of controls (Figure 4). However, methane production in sample bottles approximated or even exceeded those produced in the control bottles at the end of incubation, indicating acclimation or biodegradation of some products in the treated samples. A similar pattern was also noted for o-cresol with ozone or hydrogen peroxide as oxidant (data not shown). Ozonation products formed in the unbuffered o-cresol solutions were inhibitory even under doses as high as 24 moles/mole whereas products formed in the buffered basic solutions did not inhibit methanogenic activity under doses of 12 moles/mole or more. Lower doses of peroxide (0.3 mole/mole or less) also formed inhibitory products which exhibited inhibition during the early stages of incubation.

For 2,4-DNP, the initial compound was more inhibitory than the treated samples and progressive decrease in inhibition was observed with increasing doses of either ozone or hydrogen peroxide (Figures 5 and 6). The removal of 2,4-DNP during the course of oxidation may contribute to the observed reduction of toxicity. However, no significant reduction in toxicity was observed with permanganate oxidation in both buffered (at pH 9) and unbuffered solutions. The reduction of toxicity of 2,4-DNP by ozone or peroxide was quantified by defining relative toxicity, T_r , as

$$T_r = T/T_o$$

where

T = toxicity of samples to methane production

$$= 1 - v/V$$

T_o = toxicity of initial compound to methane production

$$= 1 - v_o/V$$

Where

v = total volume of methane produced from samples, mL

v_o = total volume of methane produced from initial compound, mL, and

V = total volume of methane produced from control, mL.

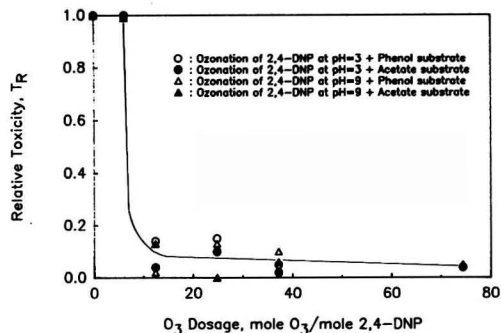


FIGURE 5. Toxicity reduction of 2,4-DNP with ozonation

Figures 5 and 6 show the toxicity of reaction products relative to the initial compound, 2,4-DNP. The reduction in toxicity by ozonation did not differ significantly between the acetate-utilizing methanogens and the phenol-degrading bacteria nor was it affected appreciably by the pH during the ozonation reaction. However, toxicity reduction by hydrogen peroxide was faster for acetate-utilizing methanogens than phenol-degraders under the same doses, indicating that the phenol-degrading bacteria were more susceptible to inhibition of the reaction products than were the acetate-utilizing methanogens (Figure 6). The doses for 50% toxicity reduction were about 2.5 moles and 4.5 moles per mole of 2,4-DNP for the methanogens and the acetogens, respectively. A dose of about 7 moles of ozone per mole of 2,4-DNP was needed to reduce toxicity to 50%. Doses beyond 5 moles H_2O_2 or 10 moles O_3 did not seem to result, appreciably, in further toxicity reduction. However, no significant toxicity reduction was noted with permanganate even under a high dose of 10 moles/mole 2,4-DNP.

Based on the oxidant doses, ozone appeared to be less efficient than peroxide or permanganate in terms of enhancing anaerobic biodegradability and performed less effectively than peroxide in reducing methanogenic toxicity. Although the gas transfer efficiency in the ozonation reactor was not determined, a low efficiency was expected, especially under the high dose conditions employed in this study. Others [24] have showed a stoichiometric yield of 2.03 moles of ozone consumed per mole of o-cresol consumed which is much lower than our values (4.1-6.1 moles O_3 /mole o-cresol). o-Cresol was much less toxic toward the methanogenic cultures than 2,4-DNP. At 300 mg/L, o-cresol was not toxic but only caused slight inhibition during the early stage of incubation. 2,4-DNP, on the other hand, ceased methanogenic activity completely even at 50 mg/L (data not shown). The observation that the phenol-degrading acetogens were more susceptible to toxicity caused by peroxide

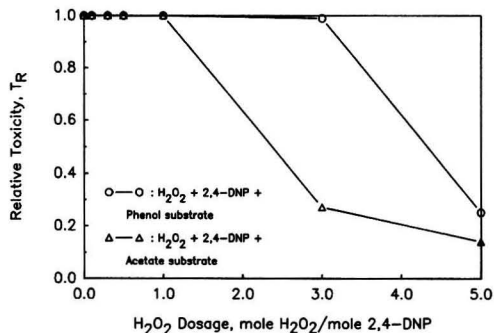


FIGURE 6. Toxicity reduction of 2,4-DNP with hydrogen peroxide

oxidation products than the acetate-utilizing methanogens (as indicated in Figure 6) is in agreement with our recent finding using substituted phenols as the test inhibitors [25]. Furthermore, ATA tests conducted on the identified, nonbiodegradable oxalic acid and glyoxylic acid revealed that these acids did not inhibit phenol degradation nor affect acetate utilization at the detected levels. Thus, the inhibition of the methanogenic cultures by oxidant treated samples may be attributed to unidentified oxidation products.

CONCLUSIONS

Chemical oxidation by ozone, Fenton's reagent, or permanganate enhanced the anaerobic biodegradability of o-cresol by forming biodegradable products such as formic acid, acetic acid, and propionic acid. However, complete or near complete oxidation of o-cresol was needed to form a significant portion of biodegradable products. The biodegradability of chemical treated o-cresol increased with increasing doses of oxidants. Chemical oxidation by ozone or peroxide also reduced the toxicity of 2,4-DNP to a phenol-enriched methanogenic culture. Based on oxidant doses, approximately 4 moles hydrogen peroxide, in the presence of a ferrous iron catalyst, 7 moles permanganate, or 25 moles ozone per mole of o-cresol is needed to significantly enhance biodegradability of o-cresol. Relatively lower doses of peroxide or ozone are required to reduce methanogenic toxicity of 2,4-DNP. The observed high doses of oxidants needed to enhance anaerobic biodegradability and reduce methanogenic toxicity may limit chemical pretreatment to small streams of industrial wastes unless oxidation efficiency can be improved through process modification or application of appropriate catalysts. However, chemical oxidation pretreatment followed by anaerobic biological processes may be applied to treat polluted groundwater in which the level of refractory and/or inhibitory contaminants are typically not high.

ACKNOWLEDGMENTS

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Soil Decontamination via Microwave and Radio Frequency Co-Volatilization

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Microwave and radio frequency heating techniques have proven to be suitable on the laboratory scale and for small scale field studies as energy sources for thermal processing of solvent contaminated hazardous waste and contaminated soils. The process described here is a technique that could be used to remove contaminants from soils or sludges on-site, collect the contaminate in an activated carbon absorption tower, and move the activated carbon off site for regeneration. The data presented show that destruction and removal efficiencies (DRE) of near 100% can be achieved for phenanthrene in simulated API separator sludge and 60% for pentachlorophenol in contaminated soil. A technique to enhance microwave absorption by the addition of carbon particles to the soil or sludge sample to be treated is discussed.

INTRODUCTION

Thermal treatment of solids contaminated with volatile hazardous constituents is a popular treatment method. Thermal treatment includes the practices of incineration, pyrolyzation coupled with incineration, or volatilization without combustion and recovery of the volatile compounds. The discussion here is limited to the noncombustion thermal treatment methods.

A commercially viable process used to remove volatile compounds, such as a mixture of petroleum derived hydrocarbons, from a contaminated solid substrate is to treat the mixture in a heated oven or rotary dryer for a period of time. This method is economical for some applications. However, regulations may prohibit direct release of contaminate laden air or exhaust gases into the atmosphere. In this case, the ability to clean the exhaust gases in order to remove contaminants becomes the limiting factor for the process.

A secondary but non-trivial problem is the heating step required to raise the temperature to a sufficient level to volatilize the contaminate. Once heated, the contaminate must diffuse through the solid particle to the surface to be removed by a sweep gas. Often, as in the case of working with heat sensitive

substrates such as polymeric materials [1], it is difficult to maintain these elevated temperatures to remove the last trace of contaminate without burning or otherwise thermally damaging the substrate. Problems occur when the outside of the substrate particle must be heated to an elevated temperature in order to effect conduction heat transfer to the center of the particle. Since microwave and radio frequency mechanisms heat from the inside out, polymeric materials can be heated without experiencing excess skin temperatures at the outside surface temperature of the particle. These techniques have been the subject of several studies [2].

The volatilization process reduces to the following operations:

1. heating the material to a temperature sufficient to remove the volatile contaminate without combustion or thermally cracking the contaminate;
2. removing the contaminate from the substrate;
3. transporting the contaminate away from the bulk of the substrate;
4. recover the substrate from an exhaust gas;
5. and dispose of the contaminate in an environmentally acceptable manner.

When dealing with materials that are considered to be haz-

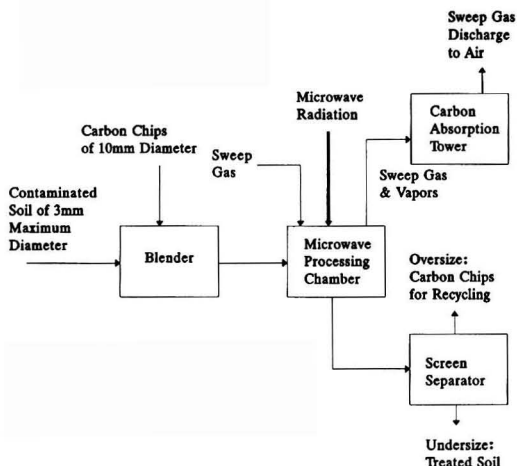


FIGURE 1. Proposed on site treatment scheme

ardous wastes, it is desirable to remove contaminants without combustion. Otherwise, the process will be classified as a hazardous waste incinerator. In the United States, incinerators have become unpopular with many environmental and political groups because of the potential for release of contaminants or by-products of combustion via the flue gas stream. Some of the by-products, such as dioxin, are perceived to be more hazardous than the original contaminants. As a result, obtaining the necessary permits to operate an incinerator is an extremely expensive and time consuming process. On the other hand, a process that does not include combustion with the associated flue gas stream will be much less controversial and should have fewer problems during the permitting process.

Dauerman and Windgasse first suggested that an inert gas could be used to protect the contaminate from exposure to oxygen while the mixture was being heated with microwave energy in a fluidized bed [3]. By eliminating oxygen, subsequent oxidation cannot take place at the elevated temperatures necessary for desorption of volatile contaminants from soils. The inert gas then acts as a carrier gas to remove volatilized compounds for recovery. The inert gas used was Argon.

Chemical Waste Management has developed a commercial process that uses conventional heating techniques for thermal desorption and recovery of volatile organic compounds. In order to avoid combustion that occurs with high temperature processing, the patented XTRACT process uses nitrogen as an inert gas to blanket the heating chamber and serve as a carrier to move the volatile compounds from the heating chamber to a cooling and recovery section [4]. The nitrogen is reheated and recycled back to the heating section and only a small amount of makeup nitrogen is needed. Nitrogen serves the purpose well as it is available commercially at a relatively low cost.

George and others [5, 6] proposed that if microwave heating is a viable technology, then the process could be carried out in a reduced pressure condition to exclude oxygen in order to prevent combustion of the contaminate. Figure 1 shows the process flow diagram proposed for the application of this microwave treatment technique. The addition of carbon particles is shown and is a technique that was used to enhance the heating of the contaminated substrate. The mechanism of this technique will be discussed later. The objective of the treatment scheme is to capture all volatile contaminants in a carbon absorption tower for off site disposal.

This technique is expanded to semi-volatile compounds in this paper. The semi-volatile compounds of interest are those commonly found in API separator sludges and contaminated soils from wood treatment sites.

API separators are used in the oil refining industry to separate solids, oil, and water from the various waste water streams generated in the refinery. These streams can be generated by a refining process, a wash down operation, tank bottom draining, or storm water runoff collection. The solid residue, API separator sludge (APISS), is a listed hazardous waste and must be disposed of as a hazardous waste unless the refinery can recycle the material back to a refining process such as a coking furnace. The sludge contains a mixture of volatile and semi-volatile compounds [7]. For the purpose of this study, phenanthrene (normal boiling point 340°C), which is found in APISS, was chosen as representative semi-volatile compound.

Additionally, tests were performed using a simulated pentachlorophenol (PCP) contaminated soil. PCP contamination is typically found in soils at wood treating sites [8].

MATERIALS AND METHODS

Figure 2 shows the apparatus used during the study. A 30 ml quartz crucible used as a sample container. The container was placed in a microwave wave guide connected to a Gerling Laboratory 1.5 kW 2450 MHz power supply. Connections were provided for nitrogen sweep gas inlet and outlet. The outlet was connected to route the entire sweep gas stream through a series of cold traps.

Contaminated substrates were placed in the crucible and heated by microwave power for a preset time interval. During the tests, a vacuum of 500 torr was maintained and sweep gas was introduced to the container at a rate of 3.3 standard liters per minute. A microwave power of 540 watts was used throughout the experiment. After heating, the substrate was removed and analyzed for contaminate.

The efficiency of microwave heating to the decontamination of the substrate was evaluated by determination of the destruction and removal efficiency (DRE) of the considered contaminate. To make this determination, the contaminate concentration in the substrate was determined before and after treatment and DRE calculated by the following equation:

$$DRE = \frac{c_i - c_f}{c_i} \times 100\% \quad (1)$$

where, c_i is the initial concentration of contaminate in the sample and, c_f is the final concentration of contaminate in the microwave treated sample.

Analysis was made in accordance with EPA standard method 8270. Direct solvent extraction was used to prepare the GC sample from the microwave treated substrate and the internal standard method was used for GC quantitative analysis. A Hewlett Packard Model 5890 Series II GC equipped with a DB-5 capillary column was used in the research.

The course of the experimental work led to the conclusion that the soil/sludge materials did not possess the dielectric characteristics necessary to absorb sufficient microwave power

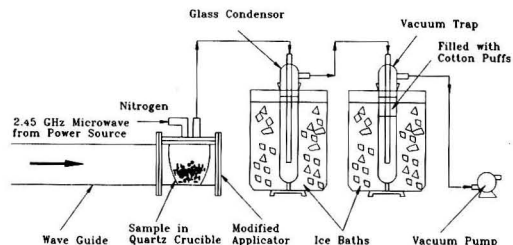


FIGURE 2. Sketch of microwave processing equipment

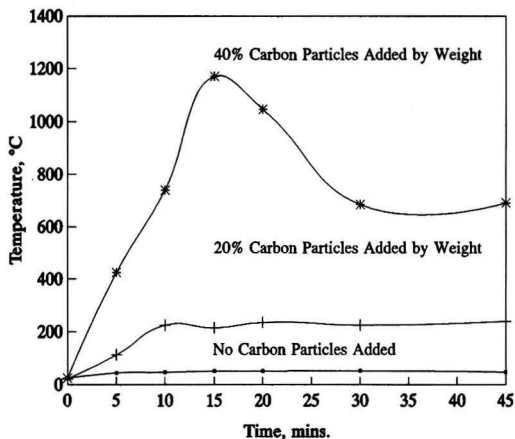


FIGURE 3. Temperature profiles of API separator sludge blank samples with carbon particles added

at a rate sufficient to maintain the temperatures required or contaminate removal. To increase the power absorption properties of the substrate, a series of experiments were performed using solid carbon particles of an average diameter of 3 mm as an admixture to the materials being treated. This technique takes advantage of the ability of carbon to absorb microwave energy by ionic conduction [9]. By using this technique, the heating of the substrate was enhanced by the carbon particle being heated by microwave energy and the substrate being indirectly heated by conduction of heat from the carbon to the substrate particle. Thus, the substrate is heated internally by microwave energy and externally by conduction from a heated carbon particle.

RESULTS AND DISCUSSION

Figure 3 illustrates the temperature rise of soil mixed with the various amounts of carbon particles added. The steady state substrate temperature without carbon particles was less than 100°C whereas the addition of a 40% admixture of carbon particles brought the test sample to a temperature in excess of 1000°C. Further power addition at temperatures above 1000°C caused physical changes in the carbon particles which decreased

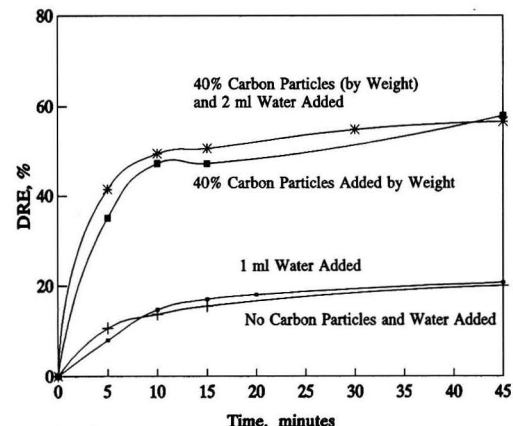


FIGURE 4. DRE of PCP in 300 PPM contaminated soil by microwave heating

its ability to absorb energy resulting in a steady state substrate temperature below 700°C. The presence of carbon particles significantly enhances the ability of the mixture to attain temperatures needed for decontamination of the soil.

A series of tests were performed to depict the effectiveness of this treatment technique to PCP removal from soils at wood treatment sites. Soil samples were spiked with 300 ppm PCP to simulate this type of contaminated soil. Figure 4 shows the PCP destruction or removal efficiency (DRE) at various operating times. About 60% of the PCP can be removed from the soil without combustion in the case of 40% added carbon particles. The DRE is rather low primarily because of the high normal boiling point of PCP (310°C).

Addition of a certain amount of water to the contaminated soil can efficiently enhance the ability of the soil to absorb microwave energy and enhance the diffusion of the volatile contaminate [6]. But this enhancement method failed for the semi-volatile contaminated soil sample shown in Figure 4 due to the fact that PCP has a much higher boiling point than water. The effect of the presence of additional volatile components is seen in the results obtained with the API separator sludge.

API separator sludge was simulated by the addition of 110 ppm of phenanthrene to a mixture of 90% 40 mesh sand and 10% heptadecane. Phenanthrene is a specific semi-volatile component of APISS whereas heptadecane is added as a control compound to simulate the presence of light oils common to APISS. The mixture was then heated in the microwave apparatus and DRE was determined. Figure 5 shows that with the addition of carbon particle, a DRE of over 99% was achieved. These results show the advantages of contaminate removal with carbon particles addition when compared to the 20% contaminate removal without carbon particle addition. Phenanthrene removal, 99%, appears to be much easier than the PCP removal, 60%, at the same conditions. Differences in normal boiling point, 340°C for phenanthrene compared to 310°C for PCP does not explain the difference in removal. The presence of the heptadecane in the phenanthrene sample probably enhanced the diffusion of the phenanthrene from the sand particles due to vapor pressure effects inside the porous substrate. Further work is planned using the addition of heptadecane to see its effect on DRE of other semi-volatile compounds in soil.

CONCLUSIONS

The data collected show that microwave heating can be used

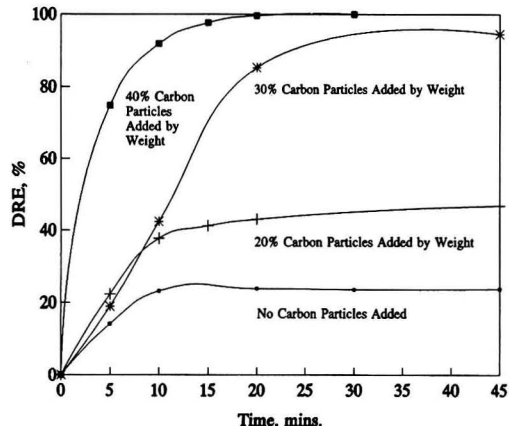


FIGURE 5. DRE of phenanthrene in API separator sludge (110 PPM) by microwave heating

to heat soil for decontamination without the use of incineration and with limited emissions of contaminants. The fact that no combustion takes place means that the chances of forming products of incomplete combustion are remote. Microwave heating has an advantage over conventional heating techniques in that it can deliver the heat energy to the inside of the heated substrate without developing excessive temperatures at the outside surface of the substrate. This is important if the substrate or the contaminate is heat sensitive.

It was found that carbon particles can effectively enhance the absorption of the heat energy. For this technique to be practical on a commercial scale, a scheme would need to be devised for the process depicted in Figure 1 whereby carbon pellets could be mixed in the soil for the heating process, recovered after the soil had been treated, and reused for the next batch of soil.

The results presented here are preliminary in nature and further study is needed. However, these preliminary results indicate that the presence of longer chain hydrocarbons, such as heptadecane, similar to those found in API separator sludge tends to enhance the removal of semi-volatiles from the sludge. This may be important if microwave heating were adopted as a commercial treatment technique.

ACKNOWLEDGMENTS

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MP&L nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

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Supercritical Extraction of Polynuclear Aromatic Hydrocarbons from Soil

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Adsorption and desorption of polynuclear aromatic hydrocarbons from soil in the presence of Supercritical CO₂ is studied. The soil adsorption isotherms are described by the Freundlich and BET models. Polar modifiers like methanol and water are found to exhibit a strong desorptive influence. A simple, single-parameter model using linear desorption kinetics is used to fit the desorption data.

INTRODUCTION

Supercritical fluid extraction is one of the most promising emerging technologies in the remediation of contaminated soils. Supercritical fluids can achieve high efficiencies in the extraction of organic contaminants from soils. Supercritical CO₂ has been demonstrated to effectively remove many species including polycyclic aromatic hydrocarbons (PAHs) [1, 2], pesticides, phenol, and polychlorinated biphenyls (PCBs) [3]. A pilot-scale extraction system has been shown to remove PCBs from contaminated sediment using liquefied propane [4]. The primary disadvantage of supercritical fluid processing is the higher equipment costs of pressure operations. However, the advantages like low operating temperature, enhanced mass transfer, and little or no solvent residue on the product can justify the capital costs, especially in smaller scale/high product value operations. Andrews [1] conducted adsorption and solubility studies focusing on four PAH compounds: anthracene, phenanthrene, triphenylene, and perylene and some desorption experiments with anthracene and phenanthrene from a sandy loam-type soil using supercritical CO₂. In this paper a simple, single-parameter model assuming linear desorption kinetics was attempted on the desorption data and found to fit with a good correlation factor.

EXPERIMENTAL METHODS

The sandy loam-type soil was packed in a pressure vessel and the system was pressurized with CO₂ using a piston pump. Recirculation of SC CO₂ fluid phase was accomplished by a magnetically coupled gear pump. On-line measurements of temperature and pressure was made using thermocouples and pressure transducers, respectively. The entire system was placed in a temperature controlled oven. On-line samples of the fluid phase were taken in a closed, 2 mL chamber using a six-port sample valve. Methanol flushing of the sample loop and trans-

fer lines assured quantitative and representative sample collection. The methanol solution containing the PAH was then analyzed by high performance liquid chromatography. Solid PAH added to the system dissolved in the circulating SC CO₂. In adsorption studies, the PAH solid was introduced below the soil bed, downstream from the recirculating flow, thus avoiding contact of undissolved solute with the soil. Adsorption took place from the solution phase only. The system volume was carefully calibrated to allow calculation of the soil PAH concentrations from the fluid phase concentrations and the mass of soil in the system. In flow desorption experiments, the soil was pre-spiked with PAH prior to desorption. The system was allowed to equilibrate with circulation for several hours. Circulation was then stopped and CO₂ was introduced at a constant flow rate. Exit flow was controlled by a heated discharge metering valve, totalized by a dry test meter, and flow rates measured by a rotameter. Samples of the post-extractor fluid were taken prior to depressurization, at frequent intervals, and then analyzed by HPLC. Complete details of the experimental procedure are given in the earlier paper [2].

PAH ADSORPTION [2]

The solubility of the PAHs in SC CO₂ was studied by using the Peng-Robinson equation of state to calculate the fluid density, and the solubility (S) behavior was shown to follow the typical van't Hoff relation, where $\ln S$ is linear with $1/T$ for constant density plots. The adsorption data were obtained at three fluid densities, and two temperatures, 45°C and 65°C. Anthracene isotherms at 45°C are shown in Figure 1. It can be seen that with increasing densities, the adsorption levels are reduced. The nonlinear, sigmoid shaped curves are nicely represented by regression to the Brunauer-Emmett-Teller (BET) isotherm equation. The Freundlich model is not able to predict the sigmoidal upswing at concentrations near the saturation limit. SC CO₂ is not a good solvent because it provides little

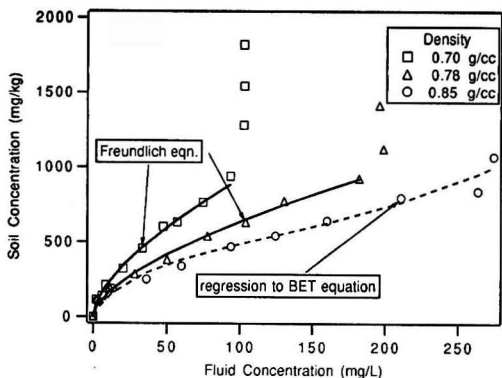


FIGURE 1. Anthracene adsorption at 45°C

polar or dispersive interaction with PAHs. However, the addition of polar modifiers can have two beneficial effects. Significant increases in PAH solubility can be achieved through the addition of a modifier such as methanol; in addition, polar modifiers can become strong competitors for polar adsorption sites in the non-aqueous SC system. To ascertain the importance of polar sites to PAH adsorption, low levels of water and methanol were added to the adsorption system during anthracene adsorption experiments. The soil was pre-equilibrated with a known concentration of anthracene, by recycling the system for several hours. After an initial sampling, water (or methanol) was added to the system in small increments and the system sampled again after re-equilibration. Figure 2 describes the effect of water or methanol on K_{ads} , the ratio of soil concentration to fluid concentration. A strong desorptive influence of both water and methanol is apparent, with the bulk of the effect occurring in the first addition of 0.2%, and a rapid decline in the desorptive effect at higher concentrations. Above 0.6%, further additions of water or methanol have only a minor effect on the adsorption of anthracene.

PAH DESORPTION

A "plug flow" desorption of the PAHs was observed. The desorption curve shapes for phenanthrene and anthracene were observed to be quite similar, with the less strongly bound phenanthrene eluting faster relative to anthracene. Tan and Liou proposed a linear desorption kinetics model [5] and found that it represented their experimental data quite well. For this work, the same model with minor modifications was utilized. The single-parameter model for describing desorption, can be

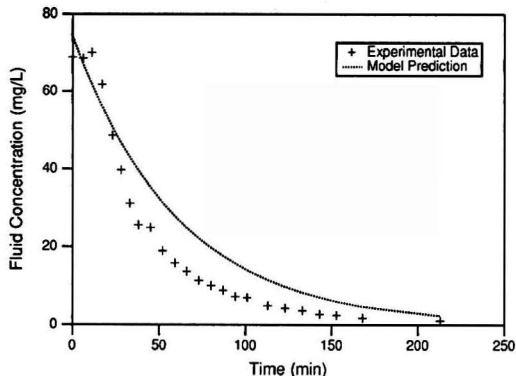


FIGURE 3. Desorption of anthracene from soil

written for the bulk fluid phase.

$$\epsilon \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial z} = -\rho_s(1-\epsilon) \frac{\partial q}{\partial t} \quad (1)$$

$$t=0, \quad C=0 \quad (2)$$

$$z=0, \quad C=0 \quad (3)$$

and for the solid phase:

$$\frac{\partial q}{\partial t} = -kq \quad (4)$$

$$t=0, \quad q=q_0 \quad (5)$$

The concentration at the exit of the bed can be expressed by:

$$C_e = \rho_s \frac{(1-\epsilon)}{\epsilon} q_0 \left\{ \exp \left[-k \left(t - \frac{\epsilon L}{u} \right) \right] - \exp(-kt) \right\} \quad (6)$$

The desorption rate constant k , was estimated by fitting Equation (6) to the experimental data. Figures 3 and 4 illustrate the observed and predicted desorption behavior of anthracene and phenanthrene, respectively. The temperature and pressure were held constant at 45°C and 2500 psig, respectively; density of SC CO₂ was 0.79 g/mL under these conditions. It can be seen that the model adequately explains the experimental observations. The desorption behavior is well correlated with the

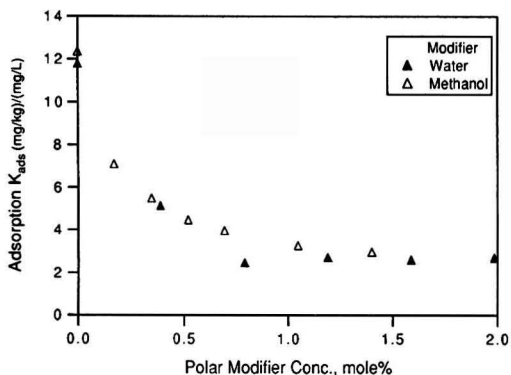


FIGURE 2. Effect of polar modifiers on anthracene adsorption SC density 0.7 g/cc

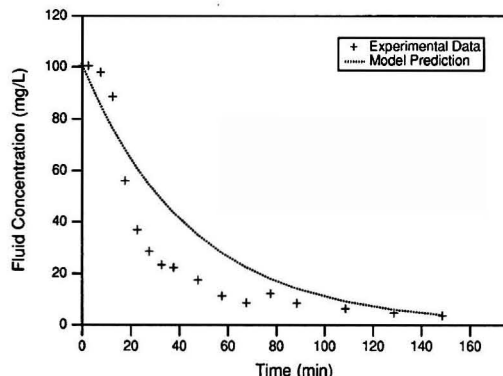


FIGURE 4. Desorption of phenanthrene from soil

model, especially at high and low PAH concentrations, with minor deviations at intermediate levels. Mass transfer resistances could possibly be responsible for the observed deviations.

CONCLUSIONS

Sandy loam adsorption isotherms for anthracene are non-linear and can be described using the BET equation. Water and methanol, added as polar modifiers in adsorption experiments, dramatically reduce the PAH adsorbed on the soil surface. A single-parameter model was used and found to explain the desorption behavior of anthracene and phenanthrene from a sandy loam-type soil, quite well. Mass transfer considerations are the focus of a current experiments and a modeling effort.

NOTATION

C = concentration of the PAH in the supercritical fluid phase, mg/L

C_e = exit concentration of PAH, mg/L

k = desorption rate constant, 1/min

L = bed length, cm

q = loaded PAH on soil, mg/Kg soil

q_0 = initially loaded PAH on soil, mg/Kg soil

t = time, min

u = superficial velocity, cm/min

z = axial position in bed, cm

ϵ = void fraction in bed

ρ_s = particle density of soil, g/cm³

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The B.E.S.T.[®] Solvent Extraction Process Treatment of Soil, Sediment, and Sludges

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Many treatment technologies are being used or proposed to remediate hazardous wastes in sites throughout the U.S. These technologies can be broken down into four general treatment categories: destructive, fixation, biological, and separation. This paper will discuss a separation technology: the B.E.S.T. (Basic Extractive Sludge Treatment) process.

INTRODUCTION

Following is a brief description of the four general treatment categories:

- **Destructive** technologies include incineration, in-situ vitrification, and selective chemical destruction (such as dechlorination of PCBs). In these types of processes the waste contaminant and other components of the waste are irreversibly changed.
- **Biological** processes are "destructive" to contaminants but since natural processes are involved, biological processes are a preferred approach for many cleanup actions if practical and economical.
- **Fixation** technologies presume that hazardous compounds in waste materials can be "locked" by mixing additives such as Portland cement that completely bind or encapsulate the waste.
- **Separation** technologies include solvent extraction, soil washing, physical separation processes (centrifugation, filtration, sedimentation and the like), and low temperature thermal desorption (drying). Thermal desorption is generally regarded as a separation process although at medium (>500°F) and high (>1000°F) operating temperatures significant irreversible changes can occur in product solid characteristics. Cracking or decomposition of organic compounds can occur.

SOLVENT EXTRACTION AS A SEPARATION PROCESS

Figure 1 is a simplified illustration of waste separation using solvent extraction. Three distinct products are produced: solids free of water and hydrocarbons, oil free of solids and water, and water without residual oil and grease or suspended solids. In the real world, none of these products will be completely free of residuals. Many design decisions are made based on the limits of the residuals allowed in each product stream. In addition, waste feeds range from watery sludges to soils highly contaminated with hydrocarbons. This further complicates design engineering decisions.

A solvent extraction process must meet the following criteria in order to process a wide variety of contaminated wastes:

- Meet treatment goals established for all decontaminated product streams
- Process a wide variety of feed compositions
- Effectively remove a broad range of organic contamination
- Meet permitting guidelines for performance and air emissions

The B.E.S.T. solvent extraction technology developed by Resources Conservation Company has been demonstrated an effective separation process for a wide variety of organically contaminated wastes in bench, pilot, and commercial scale

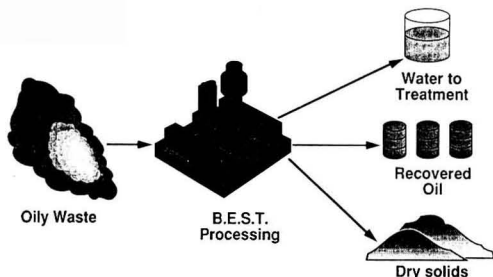


FIGURE 1. The B.E.S.T.® process.

operation. As a separation process it has been shown to effectively remove polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), pesticides, and many other organics from soil, sediment, and sludge. Current design work has focused on process design to handle a wide variety of wet and dry feeds.

THE B.E.S.T. SOLVENT EXTRACTION PROCESS

The B.E.S.T. process is a patented solvent extraction technology using triethylamine (TEA) as the solvent. TEA is an aliphatic amine that is produced by reacting ethyl alcohol and ammonia. TEA is an excellent solvent for extraction of organic contaminants from various wastes.

- TEA is easily recovered within the process due to a high vapor pressure and formation of a low-boiling azeotrope with water.
- TEA has one-seventh the latent heat of water, which allows solvent recovery at very low energy levels.
- TEA biodegrades in the environment in the presence of Aerobacter soil bacteria. (EPA document EPA-600/2-82-001a)
- TEA is inversely miscible with water; that is, soluble in water below 60°F but insoluble in water above 90°F.

The inverse miscibility property makes the B.E.S.T. process unique. A block diagram of the process is presented in Figure 2. The first extraction of the waste is conducted at 40°F. At this temperature, triethylamine is soluble with both the organics and water. The advantage of a miscible solvent is the ability to break difficult oil-water emulsions, allowing the organics to be extracted from the waste without being "protected" by the water film barrier in emulsions. The effluent from the first extraction contains most of the water in the feed material. If the first stage effluent contains sufficient water to

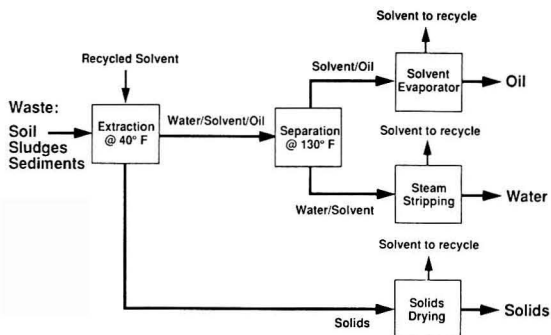


FIGURE 2. B.E.S.T. process concept.

allow a phase separation of the solvent and water, the effluent is heated to a temperature well above the miscibility limit (> 100°F). At this temperature, the effluent separates into two distinct phases, a solvent/organic phase and a water phase. The two phases are separated by gravity and decanted.

Once the water is removed, subsequent extraction stages can be conducted at elevated temperature to improve extraction efficiencies. Effluent from all stages is recovered by solvent evaporation/oil stripping and the water phase is stripped of residual solvent in a live steam stripper. Operation on waste with significant light end organics (boiling point < 200°F) such as refinery waste may require separations equipment to limit light end accumulation in the recycled solvent stream. Triethylamine is removed from the treated solids by indirect steam heating. A small amount of steam may be added directly to the dryer to improve residual stripping of solids and return a small quantity of water to the solids for dust control.

The B.E.S.T. process operates near ambient pressure and temperature and at a mildly alkaline pH. Temperatures of the liquid streams vary from about 40-170°F. The system runs at virtually atmospheric pressure. A low pressure nitrogen blanket creates a small positive pressure on tanks and vessels. Since the process operates in a closed loop, with one small vent for removal of non-condensable gases, there are virtually no air emissions. An advantage of this type of system is that it uses standard off-the-shelf processing equipment.

SEPARATION RESULTS

The B.E.S.T. solvent extraction process has been proven effective on contaminated soils, river and harbor sediment and

Table 1 PCB-contaminated soils and sediments

Test	Feed PCBs (mg./l)	% Oil	% Water	% Solids	PCBs in Solids (mg./l)	% Removal
A	250	.06	9.4	91	2.2	99.2
B	120	.06	13	87	6.4	95.4
C	4300	1.0	15	84	6.4	> 99.9
D	5300	1.0	19	80	11	99.8
E	190	.07	16	84	1.6	99.3
F	3000	1.5	30	69	0.8	> 99.9
G	15000	1.8	29	69	6.9	> 99.9
H	760	2.6	22	75	4.1	99.6
I	1900	.22	14	86	5.5	99.8
J	19	.09	16	84	0.7	96.9
K	1500	1.5	11	88	19	98.6
L	820	0.2	8	92	9.4	98.9

Table 2 Refinery "K" waste slop oil emulsion treated solids

Constituent	Feed	Product Solids	BDAT Standards
Oil & Grease, wt. %	13	0.025	—
Solids, wt. %	33	99.5	—
Benzene	100	0.0	14
Ethyl Benzene	160	0.0	14
Toluene	1300	0.044	14
Total Xylenes	1600	0.044	22
Naphthalene	340	9	42
Anthracene	47	3.6	28
Phenanthrene	190	11	34
Benzo(a)anthracene	29	2.5	—
Chrysene	22	1.6	15
Pyrene	61	3.3	36
Benzo(a)pyrene	20	2	12
Bis(2-Ethylhexyl) Phthalate	< 190	na	7.3
Di-n-Butyl Phthalate	< 190	<2.6	3.6
o-Cresol	< 190	<2.6	—
m- & p-Cresol	< 190	<2.6	—
Phenol	< 190	<2.6	3.6

various contaminated sludges. Table 1 summarizes results from many investigations of actual samples of PCB-contaminated soils from various sites. The extraction efficiencies reflected in this table are affected by the soil matrix (clay, sand, silt, etc.) and the particular process parameters (solvent to feed ratio and number of extraction stages) selected for each specific test. Achieving extraction efficiencies approaching 99% is typical.

Table 2 shows representative results from pilot tests on a difficult-to-treat refinery slop oil emulsion filter cake from the Houston area. Disposal of the solids from this material must meet strict EPA limits (BDAT standards for K048 through K052 wastes) on polyaromatic hydrocarbons (PAHs) prior to disposal in a regulated landfill. Water separated during treatment of refinery wastes is directed to the plant's waste water treatment facility while the oil separated from the waste stream is recycled back to the refinery.

Table 3 summarizes the treatment results of using the B.E.S.T. process on a soil contaminated with a wide variety of pesticide residues from a California Superfund site.

DESIGN FOR MAXIMUM FEED FLEXIBILITY

RCC has implemented several equipment design concepts in pilot and commercial scale equipment during B.E.S.T. process development. Initial pilot and commercial designs done in the

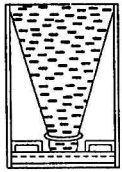
mid-80s were multi-stage, countercurrent extraction trains. Each stage employed a mix tank for feed/solvent contact and a centrifuge for separating extracted solids from the solvent containing the extracted oil and water. These designs were primarily suitable when a sludge type feed was available. Performance was quite good for sludges. Drier feeds caused excessive loading and maintenance of the centrifuges, while soils and non-pumpable feeds required front-end mixing with water, greatly increasing the amount of material that had to be treated and adding additional waste streams to the process. As the scope of the hazardous waste remediation problems became clear, the market for soils processing equipment far exceeded that for pumpable type waste streams. RCC developed a new basic design for the B.E.S.T. process that would successfully process soils but also allow pumpable sludges to be processed.

A B.E.S.T. system configured for soils and pumpable sludges and sediments uses a dual extractor design. An extractor/dryer vessel (secondary extractor) is used for direct soil extraction, solids separation and solids drying. High liquid wastes are contacted initially in a mixer/settler type extractor (primary extractor) that allows gross dewatering and organic reduction prior to transferring of the settled solids to the extractor/dryer vessel for final extraction and solids drying. All extraction is performed in a batch mode. While less elegant than a continuous process, batch extraction allows better control over extraction variables such as retention time and solvent to feed ratio and more assurance that solids meet disposal requirements.

Table 3 Pesticide contaminated soils slop oil emulsion treated solids

Constituent (mg/l)	Feed	Product Solids	Removal Eff. %
p,p'-DDT	500 mg/l	0.2 mg/l	99.96
p,p'-DDE	84	0.5	99.4
p,p'-DDD	190	0.05	99.97
Endosulfan-I	250	<0.02	>99.99
Endosulfan-II	140	<0.02	>99.99
Endrin	140	0.02	99.99
Dieldrin	37	<0.02	>99.95
Toxaphene	2600	0.9	99.97
BHC-Beta	<30	<0.13	—
BHC-Gamma (Lindane)	<30	<0.07	—
Pentachlorophenol	150	1.9	98.7

VOLUMETRICALLY



BY WEIGHT CELL

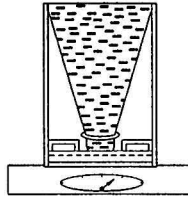


FIGURE 3(a). Soils metering.

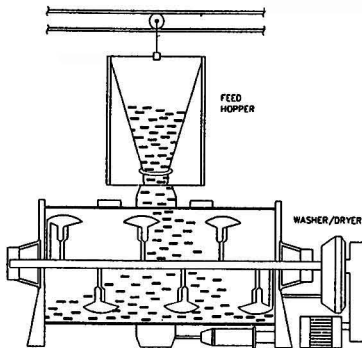


FIGURE 3(b). Washer/dryer charging.

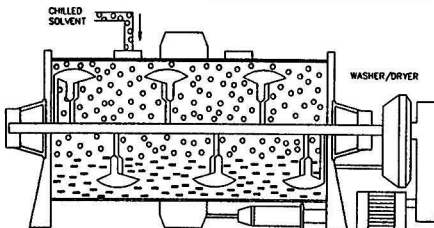


FIGURE 3(c). Solvent addition.

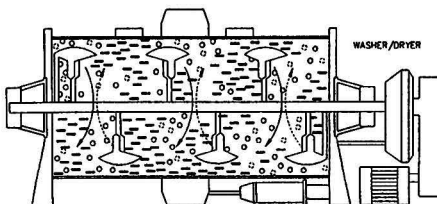


FIGURE 3(d). Extraction.

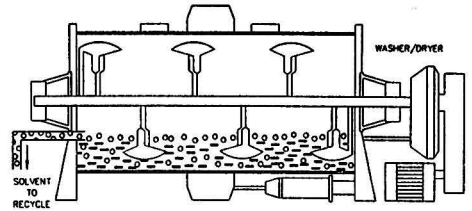


FIGURE 3(e). Solids settling and solvent draining.

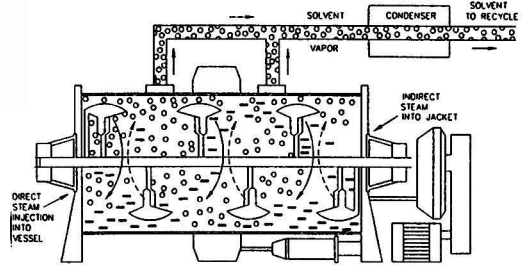


FIGURE 3(f). Solids drying.

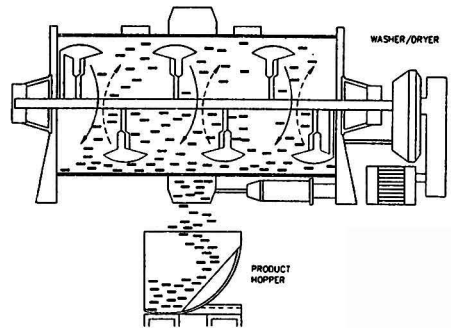


FIGURE 3(g). Solids discharging.

In soil treatment, the extractor/dryer vessel allows the contaminated soil to be handled only once. The treated solids are not moved from the extractor until the treatment level is reached. Figure 3 illustrates the typical processing sequence of a load of contaminated soil. Feed front-end handling currently includes screening to remove material greater than 1/2" in size. Extraction equipment to handle material from 1/2" to about 1 1/2"-2" is being investigated. Feed material in excess of 2" must be crushed before processing. Screened material is loaded into special transfer hopper containing about three yards of soil and transferred to the extractor/dryer vessel. The various processing steps including solvent addition, extraction/mixing, decantation, and solvent drying are identified in Figure 3.

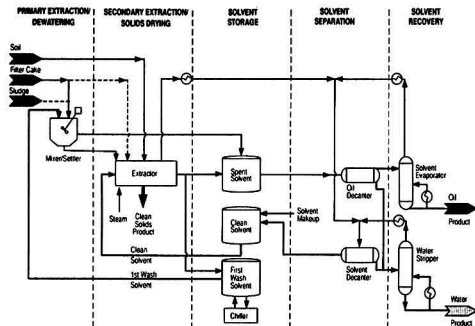


FIGURE 4. B.E.S.T. solvent extraction process.

Figure 4 shows a schematic of a B.E.S.T. unit with the dual extractor design. After each extraction step (see Figure 3) the solids are allowed to settle and the solvent mixture and particulates are separated by simple decantation of the liquid phase from the extractor vessel. Carryover of fine particulates from this step can be controlled by using a centrifuge or filter if necessary.

After each extraction step, the spent solvent is discharged to a holding tank. The spent solvent, which contains the oil and water removed from the feed, is heated to about 140°F to separate water without the expense of evaporation. The solvent phase, after water decantation, is evaporated to recycle the solvent and permit the oil product to be discharged. The recovered oil is stored for subsequent treatment, recycle, or

destruction. The water separated during decantation is steam stripped to remove residual solvent and discharged from the unit for disposal or reuse.

Upon final extraction of the solids, the extractor/dryer vessel is heated by direct and indirect addition of steam. Residual solvent is vaporized and steam stripped from the extracted solids product. Upon completion of drying the solids are discharged to a product hopper and sent to final disposal.

CONCLUSIONS

Solvent extraction using the B.E.S.T. process is a proven separation process for treatment of contaminated soils, sludges, and sediments. The B.E.S.T. solvent extraction process allows the hazardous portion of a waste to be separated and concentrated, minimizing the total waste volume and with less environmental impact than destructive technologies. The B.E.S.T. process has evolved into a highly flexible semi-batch process that can handle soil, sludges, and sediment feeds by incorporating two types of extraction concepts within a single process unit.

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Pneumatic Pumping Test for Soil Vacuum Extraction

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In-situ pneumatic pumping tests were performed to estimate the pneumatic permeability at a site containing soils contaminated with aviation gasoline. Determination of pneumatic permeability was necessary to evaluate soil-air discharge or pore volume exchange rates. Pressure propagation was measured in clustered vapor probes during the application of vacuum and positive pressure. An analytical solution for soil-air pressure distribution with a non-linear data fitting algorithm was adopted to obtain the pneumatic permeability from soil-air pressure distribution. Pneumatic pumping tests indicated substantially higher air discharge rates in the immediate vicinity of wells. The air discharge rate dissipated rapidly as distance from the wells increased. Application of increased vacuum or injection pressure resulted in substantially increased air flow in the immediate vicinity with small changes at a distance. This fact indicates that effective design should be based on air flow fields near wells, and the site specific design criteria should be determined with carefully conducted tests.

INTRODUCTION

Contamination of soils and ground water by fuels and organic solvents from leaking underground storage tanks and pipelines is common in the United States. Fuels and organic solvents contain components having low water solubilities and high vapor pressures. After initial release, they move down through the unsaturated soil zone as a non-aqueous phase liquid (NAPL), leaving residually saturated blobs in soil pores [1]. Liquid blobs trapped inside soil pores do not mobilize easily by intruding water, and limited solubilities keep them as long-term contamination sources to soil and ground water. Therefore, remediation of soil and ground water should include the removal of residual NAPL blobs from soil pores. Soil vacuum extraction (also known as soil venting) has proven to be a cost effective technology for removal of volatile organic compounds (VOCs) from residual NAPL blobs in the unsaturated soil. This in situ remediation process has been widely used in the United States since early 1980. Prior to 1980, this technology had been used primarily for methane gas control around landfills [2].

The principles of soil vacuum extraction are simple. The

evaporation of VOCs from soil pores is enhanced by artificially driven air flow. Soil vacuum extraction produces a pressure gradient, which drives air flow continuously into contaminated soils. Contaminated air is removed from subsurface soil through extraction wells and either released into the atmosphere or treated prior to discharge. A typical soil vacuum extraction system consists of extraction wells, injection wells, manifold piping, vacuum pumps, measuring gauges and controllers, and a vapor treatment system. Major advantages in soil vacuum extraction are as follows: disturbance of the contaminated soil is minimal, large volumes of soil can be treated, and standard equipment is used. Though a large number of field applications of soil vacuum extraction have been reported since early 1980, design of the field system has been empirical due to the variable field conditions and complexities of interacting processes [3, 4, 5]. Since system design is site-specific, a prototype or pilot-scale system is commonly used to obtain system parameters before full scale implementation [6]. A large number of physical and system variables are expected to impact the applicability, design, operation, efficiency, and success of the field system. Among these variables, air-filled porosity and pneumatic permeability are key parameters in controlling convective

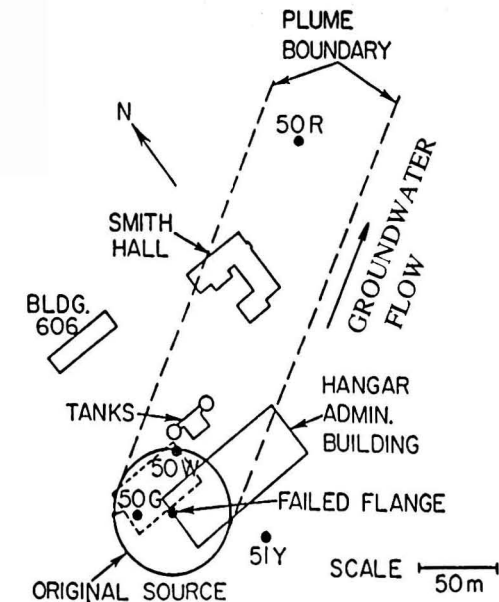


FIGURE 1. Source of Contamination and Plume Boundary at Testing Site

air flow in the unsaturated soil. Pneumatic permeability is defined as a product of the intrinsic permeability and the relative air permeability. Intrinsic permeability is defined as solely a function of soil pore structures, while relative air permeability is a function of air saturation in soil pores. When air occupies more than 80% of total porosity, relative air permeability becomes close to one for sandy soils [7].

Measurement of pneumatic permeability is well documented in the oil and gas industries [8]. Weeks [9] developed a method of determining the vertical air permeability in soils by monitoring soil-air pressure fluctuation at various depths. Jakubick [10] used a vacuum method to measure pneumatic permeability and Miller et al., [11] reported an air-injection technique to study fractures in volcanic rock. Kearn et al., [12] reported air permeability measurements of the unsaturated tuff. They used three different methods: vacuum, air injection, and laboratory testing of rock core samples. Recently, Sellers et al., [13] reported various measurement methods on soil-air permeability for soil vacuum extraction.

This paper presents a report of pneumatic pumping tests conducted at an aviation gasoline contamination site to obtain site-specific parameters for the design of a large-scale soil bioventing system. Test procedures and results are presented using two-dimensional analytical solutions of soil-air pressure distribution in a layered soil reported by Baehr and Hult [14] and Joss et al., [15].

PNEUMATIC PUMPING TEST

Site Characterization

Pneumatic pumping tests were conducted in April, 1990, at the US Coast Guard Aviation Station in Traverse City, Michigan, to obtain design parameters for a bioventing project. Contamination of soil and ground water was caused by an accidental release of aviation gasoline in the autumn of 1969. An estimated 35,000 gallons (132,000 liters) were released [16]. A plume of aviation gasoline about 260 ft (80 m) wide and 1000 ft (300 m) long existed in the ground-water flow (Figure

1). A large number of soil and ground-water samples had been collected and analyzed. Though more than twenty years had passed since the release, a sizeable fraction of the spilled fuel was found in the unsaturated zone. It had been a continuous source of ground-water contamination. A highly concentrated zone was confined in a narrow band above the water table. The surface soil at the site was categorized as a fine sand with an average grain size of 0.35 mm. Hydraulic permeability was reported as 4.6×10^{-10} ft² (4.22×10^{-7} cm²) [16]. This sand layer had a very low organic content below the top 4 inches (10 cm) of soil. The sand layer was about 47 ft (14 m) thick and was underlain by a thick clay layer. The water table was located 17 ft (5.2 m) below the soil surface when testing was conducted. Annual fluctuation of the water table was ± 2 ft (0.6 m).

Test System

Two wells, air injection and vacuum extraction, were installed 20 ft (6 m) apart in an area close to the plume. Both wells were made of schedule 40, 5-inch (12.5 cm) diameter PVC pipe with a slotted screen section at 13 to 14 ft (3.9 to 4.2 m) below the soil surface. A pressure gauge was installed at the top of each well, and those wells were connected to separate blower pumps. Ball valves were attached to connecting pipes between the wells and the blower pumps to control the pressure and air flow. All the PVC pipes were connected with glued joints. Clustered vapor probes for soil air pressure measurement were installed at various distances along the line connecting the two wells. Clusters which were at the same location with wells had to be installed 1 ft (0.3 m) away from the line. Each cluster had three probes made of 1/4-inch (6.35 mm) O.D. copper tubing with a quick release connector at the top and a 2-inch (5 cm) meshed stainless steel screen at the bottom. The depths of the probes were 3, 9, and 14 ft (0.9, 2.7, and 4.2 m) from the soil surface. A 6-inch (15 cm) diameter, hollow-stem auger was used to drill the holes for wells and probe clusters. The schematic diagram of the test system is illustrated in Figure 2. Pressures at the probes were measured with Magnahelic gauges. After the pump was started, the well pressure was adjusted by controlling the valve on the bypass lines. Soil-air pressures at the cluster probes and differential pressures on pitot tubes were measured after the well pressure was stabilized. The volumetric flow rate of air from each well was measured with a pitot tube and Magnahelic pressure gauge. For air injection, the maximum capacity of the blower pump was found to be 176 scfm (4.9 std. m³/min) at 52.3 inch H₂O (13 kPa). Due to the high permeability of the soil, pressure propagation reached steady state shortly after the pump was started. Pressure gauges in the range of less than 1 inch H₂O (0.25 kPa) were found to be very sensitive to the windy field conditions.

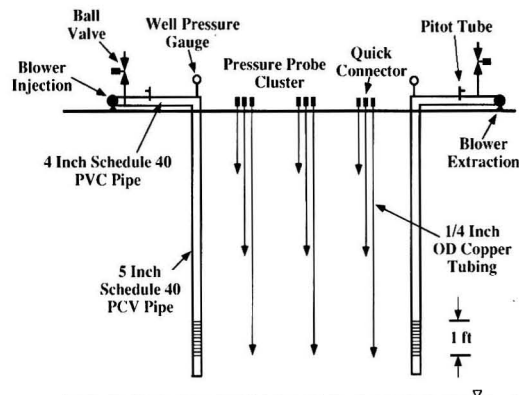


FIGURE 2. Schematic Diagram of Testing System

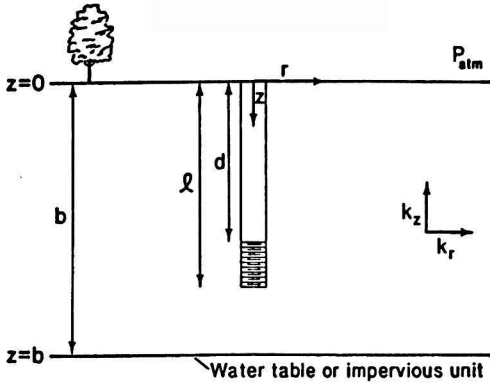


FIGURE 3. Vacuum Extraction Zone Open to Atmosphere

MATHEMATICAL MODEL

Pressure Distribution in Cylindrical Coordinate System

Baehr and Hult [14] and Joss et al., [15] presented analytical solutions to soil-air pressure distribution assuming radial symmetry around an extraction well and homogeneity in soil properties. Soil-air pressure at steady state can be described by

$$k_r \frac{\partial^2(p^2)}{\partial r^2} + k_r \frac{1}{r} \frac{\partial(p^2)}{\partial r} + k_z \frac{\partial^2(p^2)}{\partial z^2} = 0 \quad (1)$$

where k_r and k_z are pneumatic permeabilities in radial and axial directions (in this test, they are considered to be identical with horizontal and vertical directional values). The water table constitutes a lower boundary impermeable to air. A solution was obtained for the unsaturated zone with soil surface open to atmosphere as the upper boundary (Figure 3). The boundary conditions are as follows:

$$p = p_{atm} \quad \text{at } z = 0 \quad (1a)$$

$$\frac{\partial p}{\partial z} = 0 \quad \text{at } z = b \quad (1b)$$

$$p = p_{atm} \quad \text{at } r \rightarrow \infty \quad (1c)$$

at $r = r_w$,

$$\frac{\partial p}{\partial r} = 0 \quad 0 < z < d$$

$$\frac{\partial(p^2)}{\partial r} = -\frac{Q}{\pi k_r (l-d) r_w} \quad d < z < l \quad (1d)$$

$$\frac{\partial p}{\partial r} = 0 \quad l < z < b$$

The solution is

$$p^2 = p_{atm}^2 + \frac{2aQ\mu}{\pi^2 k_r (l-d) r_w} \left\{ \sum_{n=1}^{\infty} \frac{1}{m} \left[\frac{\cos\left(\frac{m\pi d}{b}\right) - \cos\left(\frac{m\pi l}{b}\right)}{M_m K_1\left(M_m \frac{r_w}{a}\right)} \right] K_0\left(M_m \frac{r}{a}\right) \sin\left(\frac{m\pi z}{b}\right) \right\} \quad (2)$$

where $m = n - 1/2$ and $M_m = (m\pi)/b$.

Specific Discharges

The specific discharges in radial and axial directions, V_r and V_z , are evaluated with Darcy's law assuming that the slip flow (Klingenberg effect) is negligible for sandy soil [14].

$$V_r = -\frac{k_r}{\mu} \frac{\partial p}{\partial r} \quad (3)$$

$$V_z = -\frac{k_z}{\mu} \frac{\partial p}{\partial z} \quad (4)$$

in which

$$\frac{\partial p}{\partial r} = \frac{1}{2p} \frac{\partial(p^2)}{\partial r} \quad (5)$$

$$\frac{\partial p}{\partial z} = \frac{1}{2p} \frac{\partial(p^2)}{\partial z} \quad (6)$$

With the relationship of the Bessel functions,

$$\frac{dK_0(r)}{dr} = -K_1(r) \quad (7)$$

the specific discharges, V_r and V_z , can be derived

$$V_r = -\frac{Q}{\pi^2 p (l-d) r_w} \left\{ \sum_{n=1}^{\infty} \frac{1}{m} \left[\frac{\cos\left(\frac{m\pi d}{b}\right) - \cos\left(\frac{m\pi l}{b}\right)}{K_1\left(M_m \frac{r_w}{a}\right)} \right] \times K_1\left(M_m \frac{r}{a}\right) \sin\left(\frac{m\pi z}{b}\right) \right\} \quad (8)$$

$$V_z = -\frac{Q}{\pi a p (l-d) r_w} \left\{ \sum_{n=1}^{\infty} \frac{1}{b} \left[\frac{\cos\left(\frac{m\pi d}{b}\right) - \cos\left(\frac{m\pi l}{b}\right)}{M_m K_1\left(M_m \frac{r_w}{a}\right)} \right] \times K_0\left(M_m \frac{r}{a}\right) \cos\left(\frac{m\pi z}{b}\right) \right\} \quad (9)$$

The analytical solutions of air pressure distribution and specific discharge were programmed for a personal computer with FORTRAN, and the program was used for simulations.

Table 1 Air Permeabilities and Soil Anisotropies (Vacuum Extraction Tests)

P _{well} (inch H ₂ O)	Air Flow (scfm)	f* (inch H ₂ O) ²	k _r (ft ²) × 10 ¹⁰	k _z (ft ²) × 10 ¹⁰	Anisotropy (k _r /k _z)
-50	-132	3.18	9.75	2.17	4.49
-50	-117	2.99	8.62	1.94	4.44
-42	-100	2.32	8.48	2.10	4.03
-36	-83	1.05	7.81	2.37	3.29
-24	-68	0.44	9.44	2.74	3.44
-20	-57	0.23	9.09	3.21	2.83
-16	-57	0.11	11.38	3.81	2.99
Averaged Value			9.22	2.53	3.64
Std. Deviation			1.15	0.68	0.68

f*: value of equation (10)

Parameter Estimation by Non-linear Least Square Data Fitting

Two unknown parameters, pneumatic permeabilities, k_r and k_z , can be obtained by a non-linear data fitting method [17]. The method adopts a pseudo-Newtonian algorithm to search the multivariable values which minimize the objective function. In this study, the objective function is defined as

$$f = \sum_i^N (p(r_i, z_i) - p_i)^2 \quad (10)$$

where $p(r_i, z_i)$ is the estimated pressure at the observation point (r_i, z_i) with equation (2), p_i is the observed pressure at the point (r_i, z_i) , and N is the number of observation points. For each test, 16 observation point data, including the well pressure, were used.

RESULTS AND DISCUSSION

A series of vacuum extraction, air injection, and combined operation tests were conducted. Permeabilities obtained from vacuum extraction and air injection tests are listed in Tables 1 and 2. Directional permeabilities obtained in both tests show a reasonable consistency within one standard deviation. The horizontal permeabilities obtained from air-injection tests show slightly higher values than those from vacuum extraction tests, and the vertical permeabilities show lower values. From these differences, anisotropic ratios from air injection tests become ten times higher than those from vacuum extraction tests. In general, permeabilities obtained from pneumatic pumping tests agree reasonably well with the hydraulic permeability value of 4.6×10^{-10} ft² (4.2×10^{-7} cm²) reported by Ostendorf et al. [16] and the pneumatic permeability, 3.5×10^{-10} ft² (3.2×10^{-7} cm²), which was estimated from the particle size of $D_{15} = 0.16$ mm [18].

Figure 4 shows the pressure distributions at three different depths. The well pressure was -50 inch H₂O (-12.4 kPa) and the air flow rate was 132 scfm (3.68 std. m³/min). The solid lines were generated by substituting pneumatic permeabilities,

$k_r = 9.8 \times 10^{-10}$ ft² (8.9×10^{-7} cm²) and $k_z = 2.2 \times 10^{-10}$ ft² (2.0×10^{-7} cm²), into equation (2).

A large pressure gradient and air flow are expected near the well, with a corresponding decrease as the distance from the well increases. In order to define the effective zone of a well, the radial discharges, V_r , at 14 ft (4.2 m) depth with two well pressures were calculated and are plotted in Figure 5. The radial discharge at the well screen is 8.8×10^3 ft/hr (2.7×10^3 m/hr) for -50 inch H₂O (-12.4 kPa) well pressure. The specific discharge is reduced to 50 ft/hr (15 m/hr) at 15 ft (4.5 m) and 1.2 ft/hr (0.36 m/hr) at 30 ft (9 m) from the well. The specific discharges with smaller vacuum (-16 inch H₂O) also show the similar trend of decrease, but in a moderate rate. Volumetric flow rates and well vacuum pressures are plotted in Figure 6 which shows a linear correlation. A larger vacuum in the well can produce higher discharges at close vicinity around the well than the smaller vacuum application, but their differences are reduced rapidly as the distance increases from the well. It seems that increased vacuum application in the well does not provide a significant increase on the radius of influences in the unsaturated zone open to the atmosphere.

SUMMARY AND CONCLUSIONS

From the pilot-scale test, pneumatic permeabilities at the aviation gasoline spill site could be obtained. Permeability estimations could be achieved by using an analytical solution of the pressure distribution and a non-linear data fitting algorithm. Some degrees of anisotropy were observed in soils. Estimated pneumatic permeabilities were in a reasonable agreement with previously reported hydraulic permeabilities.

Concerning pumping efficiency, various factors should be considered in the design of a full-scale operation. Even with high vacuum in the well, most air flow is limited to the immediate vicinity of the well. The VOC removal rate within a short distance from the well is expected to be rapid and much slower at greater distances. Therefore, a single well with high pressure removes VOCs nonuniformly from the contaminated area and may not be efficient to clean up a wider area. The cleanup time depends on the amount of direct air flow through the contaminated soils. Prior to the initiation of a full-scale

Table 2 Air Permeabilities and Soil Anisotropies (Air Injection Tests)

P _{well} (inch H ₂ O)	Air Flow (scfm)	f* (inch H ₂ O) ²	k _r (ft ²) × 10 ¹⁰	k _z (ft ²) × 10 ¹⁰	Anisotropy (k _r /k _z)
44	174	13.7	16.1	0.569	28.3
36	158	11.0	18.4	0.563	32.7
24	113	7.33	21.7	0.386	56.2
16	71	2.81	20.2	0.459	43.6
Averaged Value			19.1	0.494	40.2
Std. Deviation			2.41	0.088	12.5

f*: value of equation (10)

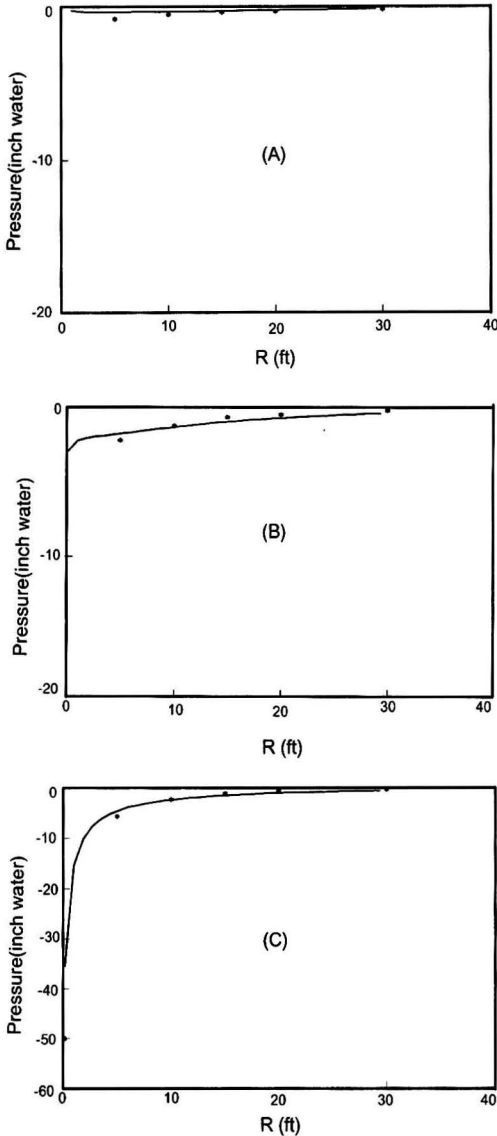


FIGURE 4. Soil-Air Pressure Distributions, $p_{well} = -50$ inch H_2O , (—) estimated from equation (2), (*) measured values, (A) depth = 3 ft, (B) depth = 9 ft, (C) depth = 14 ft

design, a pilot-scale pneumatic pump test provides valuable information on optimum parameters. Additional tests, such as tracer gas injections, will be useful to verify the parameters.

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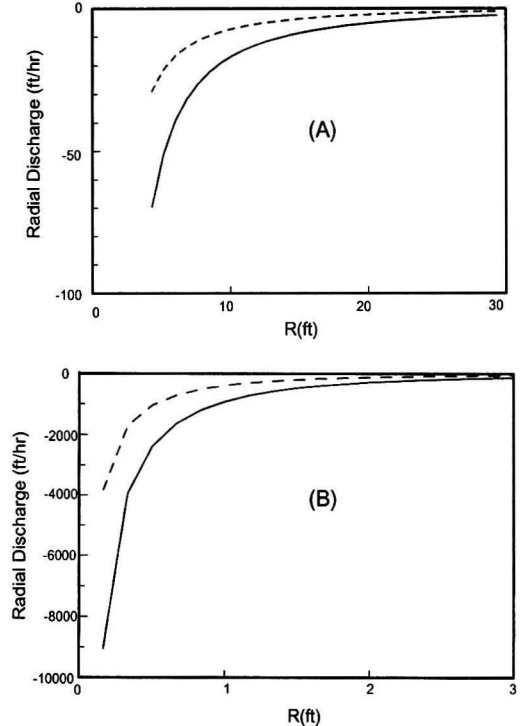


FIGURE 5. Specific Discharges in Radial Direction, (—) $p_{well} = -50$ inch H_2O , (---) $p_{well} = -16$ inch H_2O , (A) $r_w \geq 3$ ft, (B) $r_w < r < 3$ ft

ment of the system design or trade names should be inferred. The reported testing was not conducted under an approved Quality Assurance Project Plan.

NOTATION

- a = square root of anisotropy ratio $(k_r/k_z)^{1/2}$
- b = depth to water table from soil surface
- d = depth to the top of well screen from soil surface
- k_r = pneumatic permeabilities in radial (horizontal) direction

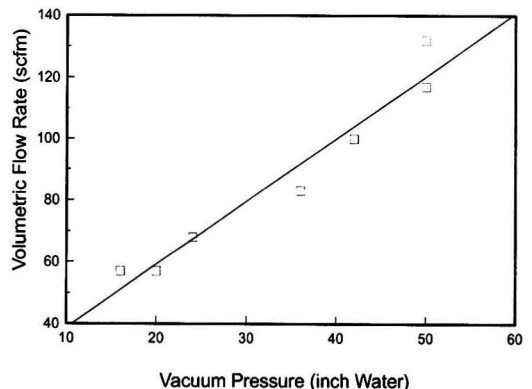


FIGURE 6. Volumetric Flow Rates vs. Extraction Well Vacuum

k_z = pneumatic permeabilities in axial (vertical) direction
 K_0 = the zero-order modified Bessel function of the second kind
 K_1 = the first-order modified Bessel function of the second kind
 l = depth to the bottom of well screen from soil surface
 N = Number of observation point data used in data fitting
 p = soil air pressure
 p_{atm} = atmospheric pressure
 $p(r_i, z_i)$ = estimated pressure at location i (r_i, z_i)
 p_i = observed pressure at location i
 Q = volumetric flow rate at standard state
scfm = standard cubic feet per minute
 V_r = specific discharge in radial (horizontal) direction
 V_z = specific discharge in axial (vertical) direction
 μ = viscosity of air

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Adsorption/Desorption Characteristics of Lead on Various Types of Soil

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Laboratory studies were conducted to address the phenomena of adsorption/desorption of lead onto various types of soils, both in the absence and presence of the chelating agent, ethylenediaminetetraacetic acid (EDTA). The linear and Freundlich isotherm models provided adequate description of the adsorption/desorption behavior. Over the range of EDTA concentrations employed in the study (0.1 to 0.10M), no significant difference in the isotherm parameters was observed as a result of the applied EDTA concentration. The presence of EDTA significantly altered the adsorption/desorption behavior of lead on the soil, resulting in less of the metal being adsorbed. The soil with the higher silt/clay content had a greater amount of lead adsorbed onto it (as compared with the sandy soil).

BACKGROUND

The contamination of soils by heavy metals has resulted from a number of activities, including vehicle emissions; mining, smelting, and metal plating/metal finishing operations; automobile battery production; application of industrial waste, fertilizers, and pesticides; and fly-ash from incineration/combustion processes. Reported ranges of heavy metal concentrations from various soils are summarized in Table 1.

Heavy Metal Removal Techniques

Techniques for removal of metals from soil generally involve bringing the soil into contact with an aqueous solution. Such methods as flotation and waste classification are solid/liquid separation processes. Metal contamination is generally found on the finer soil particles, so separating the finely divided material may substantially reduce the heavy metal content of the bulk soil. Separating the fines from the coarse fraction was found to remove 90% of the metals but only 30% of the total dredged material [9]. In flotation processes, metallic minerals become attached to air bubbles that rise to the surface, forming a froth and thereby being separated from particles that are wetted by water [10]. Although flotation has been successfully used in the mineral processing industry, it has not been widely

used for the treatment of contaminated soils [11]. Solid/liquid separation processes represent a preliminary step in the remediation of contaminated soils. The metals are still bound to a solid phase, but in a much more concentrated form. The advantage of this preliminary processing step is that the mass of contaminated soil to be processed is reduced considerably; therefore, the treatment cost is reduced.

Pickering [12] identified four approaches whereby metals could be mobilized in soils: (1) changing the acidity, (2) changing the system ionic strength, (3) changing the oxidation/reduction (REDOX) potential, and (4) forming complexes. In the last technique, the addition of complexing ligands can convert solid-bound heavy metal ions into soluble metal com-

Table 1 Reported Heavy Metal Concentrations

Heavy Metal	Site Type	Reported Concentration Range (ppm)	Reference
Zn	Smelting	26,000-80,000	[1]
Cd	Smelting	900-1,500	[1]
Cr	Chromium Production	500-70,000	[2]
Pb	Battery Reclamation		
	Soil	2-135,000	[3, 4]
	On-Site Sediment	2.16-42,700	[3, 4]
	Surface Water	0-140 mg/L	[5]
Pb	Battery Recycling		
	Soil	210-75,950 mg/kg	[6]
	Soil	0-211,300mg/kg	[7, 8]

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Table 2 Properties of Chelating Agents

Chelating Agent	Molecular Weight	Acidity Constants					Log of the Stability Constant for the Metal Chelate					
		pK ₁	pK ₂	pK ₃	pK ₄	pK ₅	Cd	Zn	Cu	Pb	Mn ⁺⁺	Fe ⁺⁺⁺
NTA ^a	191	1.89	2.49	9.73	--	--	10.5	11.2	13.7	11.8	8.1	17.0
EDTA ^b	292	2.08	3.01	6.40	10.44	--	17.5	17.2	19.7	17.7	14.5	26.5
DTPA ^c	393	2.08	2.81	4.49	8.73	10.6	20.1	19.7	22.6	21.0	16.7	29.2

^aNitrilotriacetic acid.

^bEthylenediaminetetraacetic acid.

^cDiethylenetriaminepentaacetic acid.

plexes. The effectiveness of complexing ligands in promoting the release of metals depends on the strength of bonding to the soil surface, the stability and adsorbability of the complexes formed, and the pH of the suspension [11]. From an application viewpoint, the type and concentration of the complexing ligand and the system pH are the operational parameters that can be controlled.

The ability of chelating agents to form stable metal complexes makes materials such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) promising extractive agents for the treatment of soils polluted with heavy metals [13]. Elliott and Peters [11] have noted that although complexation is the major mechanism responsible for the metal solubilization, the overall release process depends on the hydrogen ion concentration and the system ionic strength. Because hydrous oxides of iron and manganese can coprecipitate and adsorb heavy metals, they are believed to play an important role in the fixation of heavy metals in polluted soils [14]. Their dissolution under reducing conditions may weaken the solid heavy-metal bond and thereby promote solubilization of the metal ions. Elliott and Peters [11] noted that there are five major considerations in the selection of complexing agents for soil remediation:

- (1) Reagents should be able to form highly stable complexes over a wide pH range at a 1:1 ligand-to-metal molar ratio.
- (2) Biodegradability of the complexing agents and metal complexes should be low (especially if the complexing agent is to be recycled for reuse in the process).
- (3) The metal complexes that are formed should be non-adsorbable on soil surfaces.
- (4) The chelating agent should have a low toxicity and low potential for environmental harm.
- (5) The reagents should be cost effective.

Elliott and Peters [11] note that, although no compounds ideally satisfy all these criteria, there are several aminocarboxylic acids that form remarkably stable complexes with numerous metal ions. The properties of three chelating agents that have been used to extract contaminants from soil (either for analyses or remediation) are summarized in Table 2.

Extraction of heavy metals from contaminated soils can be performed by either using *in-situ* techniques or on-site extraction (following excavation). In the case of *in-situ* soil flooding, the aqueous extractive agent is allowed to percolate through the soil to promote metal mobilization. In the case of on-site extraction following excavation, the operation can be performed on a batch basis, semi-batch basis, or continuously. The contaminated soil is first pretreated for size reduction and classification and then brought into contact with the extractive agent. Finally, the soil is separated from the spent extractive agent, and the effluent is further recycled to decomplex and precipitate the heavy metals from solution. Alternatively, the solution is treated by using electrodeposition techniques to recover the heavy metals.

Adsorption Isotherm Characterization

The adsorption of heavy metals onto soil was examined by application of three commonly used adsorption isotherm models: the linear, Langmuir, and Freundlich models. Equations describing these models are listed below:

$$\text{Linear: } q_e = kC + q_{e,0} \quad (1)$$

$$\text{Langmuir: } q_e = \frac{Q^0 b C}{1 + b C} \quad (2)$$

$$\text{Freundlich: } q_e = K_N C^{1/n} \quad (3)$$

where q_e is the amount of solute (heavy metal) adsorbed per unit weight of adsorbent, C is the measured solute concentration in solution at equilibrium, Q^0 is the amount of solute adsorbed per unit weight of adsorbent in forming a complete monolayer coverage on the adsorbent (soil) surface, b is a constant related to the net enthalpy of adsorption, and k , K_N , and $q_{e,0}$ are empirical constants.

These equations are linearized using the equations listed below.

$$\text{Linear: } q_e = kC + q_{e,0} \quad (4)$$

$$\text{Langmuir: } \frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0} \frac{1}{C} \quad (5)$$

$$\text{Freundlich: } \ln q_e = \ln K_N + \frac{1}{n} \ln C \quad (6a)$$

or

$$\log q_e = \log K_N + \frac{1}{n} \log C. \quad (6b)$$

GOALS AND OBJECTIVES

The primary goal of this project was to determine and compare the performance of several chelating agents [ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA)] for their ability to extract lead (Pb) from contaminated soil. The focus of this paper is to determine the adsorption/desorption behavior of lead onto several soil types using EDTA as the extractant.

Table 3 Characteristics of the Soils Used in the Adsorption/Desorption Studies

Type	pH	Texture	Classification (wt %)		
			Sand	Silt	Clay
A	7.75	Silty clay	14.6	39.0	46.4
B	---	Loamy sand	78.5	12.2	9.3

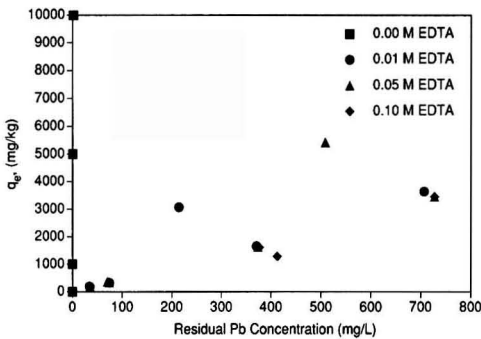


FIGURE 1. Characteristics of lead adsorption onto Soil A in the presence of EDTA

EXPERIMENTAL PROCEDURE

The laboratory experiments were performed using a batch shaker technique to investigate the adsorption/desorption behavior of lead onto various soil types. The experimental procedure associated with the adsorption and desorption studies are described below.

Adsorption Studies

Uncontaminated soil was prepared by grinding the soil with a ceramic mortar and pestle until the ground soil could pass through a 850- μm (ASTM mesh No. 20) sieve. The initial characteristics of the two different soil types are summarized in Table 3. Each soil type was spiked (artificially contaminated) with a solution of lead nitrate and left in contact for a 3.0-hour time period on the shaker table. Nominal initial lead concentrations applied to the soil were 500, 1000, 5000, and 10,000 mg/kg soil. The soil was weighed in 5-gm portions using a top-loading balance and placed in plastic, lidded shaker containers. To these containers, 45 mL of a EDTA solution was added. Replicate samples were prepared on every fourth sample. The EDTA concentrations of the extracting solution were nominally 0, 0.01, 0.05, and 0.10 M. This matrix of initial lead and EDTA concentrations enabled the adsorption/desorption characteristics of lead onto the various soil types to be described both in the absence and in the presence of EDTA.

The soil samples (to which the metal and extracting agent had been added) were shaken for 3 hours at a low setting on an Eberbach shaker table. This time requirement was determined on the basis of preliminary experiments in which the

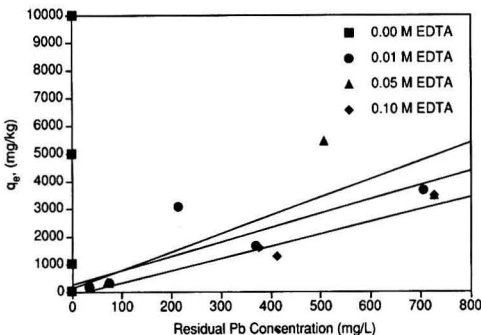


FIGURE 2. Linear isotherm for lead adsorption onto Soil A in the presence of EDTA

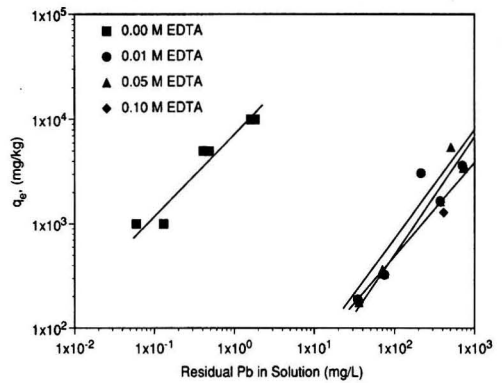


FIGURE 3. Linearized Freundlich isotherm for lead adsorption onto Soil A in the presence of EDTA

residual concentration was monitored as a function of time on the batch shaker table [15]. This analysis showed that chemical equilibrium could be achieved within 3.0 hours. Following agitation, the samples were centrifuged in plastic Nalgene centrifuge tubes equipped with snap-on caps, filtered using No. 42 Whatman filter paper, and stored in glass vials maintained at $\text{pH} < 2$ (prepped using HNO_3) prior to atomic absorption spectroscopy (AAS) analysis. The Buck Scientific Atomic Absorption/Emission Spectrophotometer, Model 200-A, was calibrated using AAS lead standards. The lead analyses were performed in accordance with standard procedures [16]. The residual lead concentration remaining in solution was determined from the AAS analyses. The amount of lead adsorbed per unit weight onto the soil (for each concentration of EDTA) was determined using the difference between the initial concentration of the solution applied to the soil and the final residual concentration after treatment. Using the different initial lead concentrations, the adsorption isotherms were determined using the linearized isotherm equations presented in equations (4) through (6).

Desorption Studies

Uncontaminated soil was again prepared by grinding the soil with a ceramic mortar and pestle to enable the soil to pass through a 850- μm sieve. Each soil sample was spiked with a different lead nitrate concentration (nominally 500, 1000, 5000, and 10,000 mg/kg soil, which were assumed to be the initial

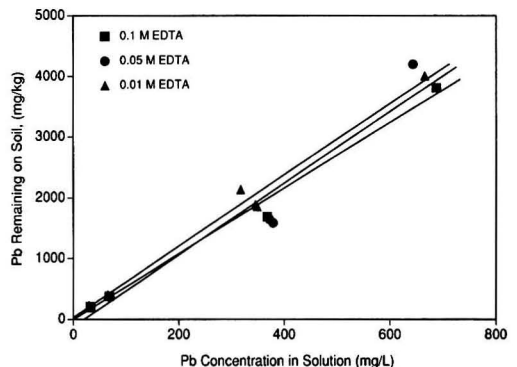


FIGURE 4. Linear isotherm desorption characteristics for lead from Soil A using EDTA as the extractant

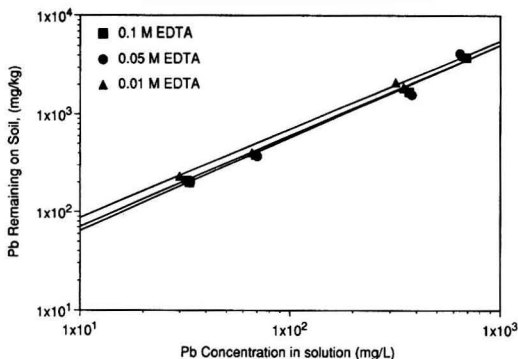


FIGURE 5. Linearized Freundlich desorption isotherm for lead from Soil A using EDTA as the extractant

lead concentrations on the soil samples) and left to air dry. Concentrations were checked by AAS analysis of nitric acid extractions of the soil. The contaminated soils were then aged in glass jars (with screw-on covers) for approximately three months prior to performing the desorption experiments.

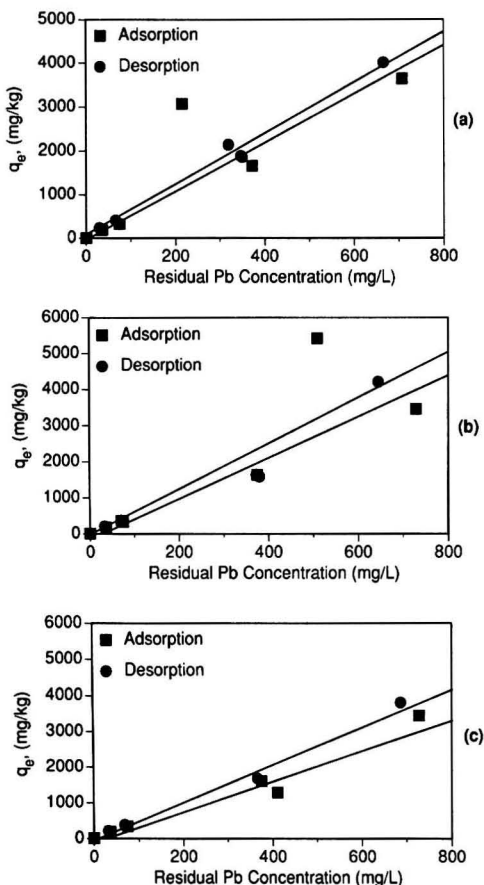


FIGURE 6. Comparison of the adsorption/desorption characteristics of lead onto Soil A for EDTA concentrations of (a) 0.01 M, (b) 0.05 M, (c) 0.10 M

Table 4 Linear Adsorption/Desorption Isotherm Model for Lead onto Soil Type A

EDTA Concentration (moles/L)	Adsorption		Desorption	
	k (L/kg)	$q_{e,0}$ (mg/kg)	k (L/kg)	$q_{e,0}$ (mg/kg)
0.00	5570	335	--	--
0.01	5.40	107	5.90	10.5
0.05	6.28	17.4	5.96	-152
0.10	4.43	-46.7	5.38	-20.7

These contaminated soils were then weighed in 5-gm portions using a top-loading balance and placed in plastic containers that had lids. To these containers, 45 mL of an EDTA solution (or deionized water) was added. The procedure for determining the adsorption isotherms then follows that described for the adsorption studies.

RESULTS AND DISCUSSION

Figure 1 presents the adsorption characteristics of lead onto Soil A for various EDTA concentrations ranging from 0 to 0.10 M. Figures 2 and 3 present the linearized isotherms using the linear and Freundlich isotherm models. The Langmuir model did not adequately describe the adsorption of lead onto the various soils due to the fact that negative values of Q^0 and b were obtained from the linearization of several Pb/EDTA combinations.

Figure 4 presents the desorption characteristics of all three EDTA concentrations on Soil A using the linear adsorption model. All three EDTA concentrations resulted in nearly the same desorption characteristics. Figure 5 presents the linearized Freundlich isotherm for the three EDTA concentrations. The slopes of the resulting lines are nearly equal, indicating the desorption behavior is independent of the EDTA concentration over the limited range of EDTA concentrations used in this study (0.01 to 0.10 M).

Figures 6a through 6c compare the adsorption/desorption characteristics for the lead remaining on Soil A for EDTA concentrations of 0.01, 0.05, and 0.10 M, respectively. These plots did not indicate significant differences in the adsorption/desorption characteristics on Soil A. Tables 4 through 6 show the adsorption/desorption isotherms using the linear, Freundlich, and Langmuir isotherm models. The values of k for the linear isotherm and K_N and $1/n$ for the Freundlich isotherm models are similar for both the adsorption and desorption studies. Statistical analyses were conducted, and t -tests performed on the differences in the mean values were not significant at a 0.9 level of significance, showing the common behavior of the adsorption and desorption systems. As described earlier, the Langmuir isotherm model does not adequately describe the adsorption of lead onto soil because negative values of Q^0 and b were obtained for the EDTA concentrations of 0.01 and 0.05 M.

Table 5 Freundlich Adsorption/Desorption Isotherm Model for Lead onto Soil Type A

EDTA Concentration (moles/L)	Adsorption		Desorption	
	$1/n$	K_N	$1/n$	K_N
0.00	0.71	4760	--	--
0.01	1.05	4.69	0.92	9.44
0.05	1.10	3.30	0.95	7.05
0.10	0.93	6.29	0.94	7.58

Table 6 Langmuir Adsorption/Desorption Isotherm Model for Lead onto Soil Type A

EDTA Concentration (moles/L)	Adsorption		Desorption	
	Q^o	b	Q^o	b
0.00	1790	15.6	--	--
0.01	-26,800	-0.00019	6130	0.00127
0.05	-30,900	-0.00016	5920	0.00105
0.10	5340	0.00096	6930	0.00092

One striking feature noted from inspection of Tables 4 and 5 is the drastic change in adsorption behavior associated with the presence of EDTA. The value of k for the linear isotherm model is nearly 1000 times larger with no EDTA present as compared with the case when EDTA is present. Similarly, for the Freundlich model, the parameter K_n is likewise nearly 1000 times greater for the case of no EDTA present versus the case where EDTA is present. The exponent $1/n$ is least 24% lower for the case of no EDTA present versus EDTA being present. A value of $1/n < 1$ indicates a strong affinity for adsorption. Thus, the presence of EDTA as a complexing agent decreases the affinity for lead to adsorb onto the soil, resulting in an inhibition to lead adsorption.

Furthermore, the extraction of lead from this soil type using EDTA was pH-insensitive over the pH range of 4 to 12 [15, 17]; the removal of lead ranged from 58% to 64% over the entire range of initial lead concentrations. Also, the applied EDTA concentrations over the range of 0.01 to 0.10 M had little effect on the removal efficiency of lead from the soil [15, 17].

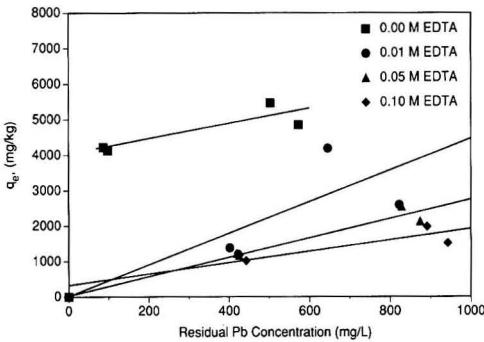


FIGURE 7. Linear isotherm for lead adsorption onto Soil B in the presence of EDTA

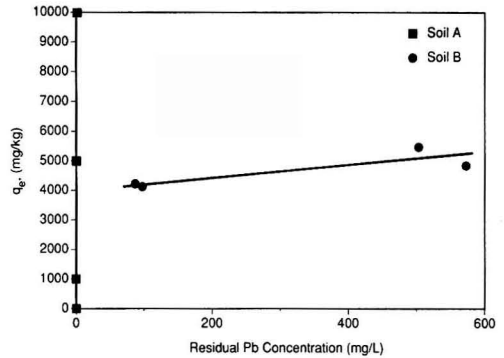


FIGURE 9. Comparison of the adsorptive behavior of lead onto Soils A and B with no cheating agents present using the linear isotherm model

Figure 7 presents the adsorption characteristics onto Soil B for EDTA concentrations ranging from 0 to 0.10 M. This figure once again indicates a much higher amount of lead adsorbed onto the soil in the absence of EDTA as compared to the amount of lead adsorbed in the presence of EDTA. Figure 8 presents the analogous adsorption characteristics of lead onto Soil B using the Freundlich isotherm model. All three EDTA concentrations result in nearly identical values of the exponent, $1/n$.

Figure 9 compares the adsorptive characteristics of lead onto the two soil types, A and B, for the case of no chelants being

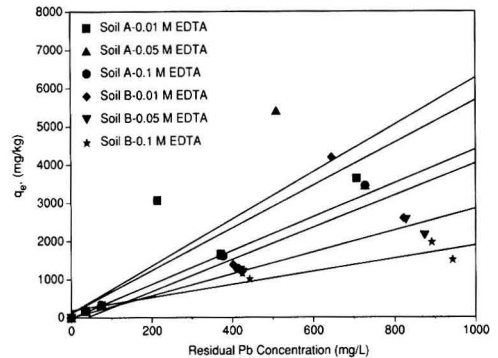


FIGURE 10. Comparison of the adsorptive behavior of lead onto Soils A and B in the presence of EDTA using the linear isotherm model

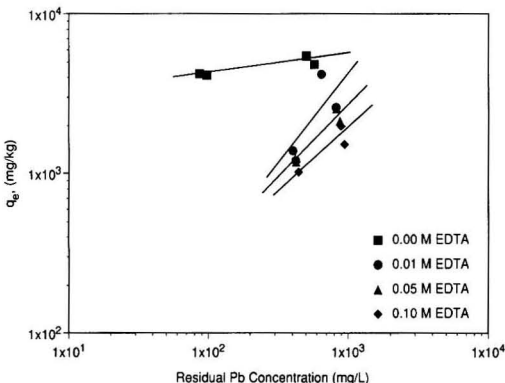


FIGURE 8. Linearized Freundlich isotherm for lead adsorption onto Soil B in the presence of EDTA

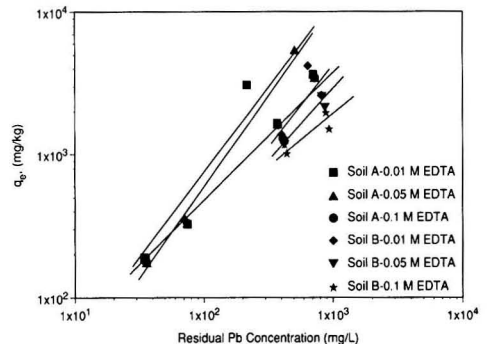


FIGURE 11. Comparison of the adsorptive behavior of lead onto Soils A and B using the Freundlich isotherm model

Table 7 Comparison of Linear Lead Adsorption onto Soil Types A and B in the Presence of EDTA

EDTA Concentration (moles/L)	Soil Type A		Soil Type B	
	<i>k</i> (L/kg)	<i>q_{e,0}</i> (mg/kg)	<i>k</i> (L/kg)	<i>q_{e,0}</i> (mg/kg)
0.00	5570	335	5.68	2310
0.01	5.40	107	4.20	- 53.5
0.05	6.28	17.4	2.71	36.1
0.10	4.43	- 46.7	1.78	175

present. The adsorptive capacity for lead is much, much greater for the case of Soil A, due to the much larger silt/clay fraction for Soil A as compared with Soil B. Because Soil B is more sandy, the amount of lead adsorbed onto the soil remains relatively constant over large residual lead concentrations in solution. Figure 10 compares the adsorptive characteristics of lead onto the two soil types in the presence of EDTA. Once again, the adsorptive capacity of lead is much larger (generally 2-3 times larger) on Soil A as compared with Soil B due to the larger silt/clay fraction. Heavy metals are known to preferentially bind to clays and humic materials [9]. Figure 11 presents the analogous description of the adsorptive behavior of lead onto the two soil types in the presence of EDTA using the Freundlich isotherm model. The amount of lead adsorbed onto Soil A is typically about 0.5 order of magnitude larger than the amount of lead adsorbed by Soil B under comparable experimental conditions. Tables 7 and 8 compare the adsorptive behavior of Soils A and B using the linear and Freundlich isotherm models, respectively.

SUMMARY AND CONCLUSIONS

These laboratory studies investigated the adsorption/desorption phenomena for lead onto two soil types. Soil A had a high silt and clay content (~85%), whereas Soil B had a very high sand content (>78%). The adsorption/desorption phenomena was studied for various initial lead concentrations, ranging from 500 to 10,000 mg/kg soil; these studies were performed both in the presence and absence of EDTA. The linear and Freundlich isotherm models provide an adequate description of the adsorption/desorption behavior of lead onto these two soil types. In contrast to this behavior, the Langmuir isotherm model did not provide an adequate description of this behavior, due to values of *Q^o* and *b* obtained in the isotherm linearization having negative values.

There was no significant difference in the adsorption/desorption characteristics of lead on either soil for EDTA concentrations in the range of 0.01 to 0.10 M. The presence of EDTA, however, significantly altered the adsorption/desorption characteristics of lead onto both soil types. The presence of EDTA resulted in less of the metal being adsorbed onto the soil due to the strong complexing ability of the chelating agent.

There was a significant difference in the adsorptive behavior of lead onto these soils, which is postulated to be due to the

Table 8 Comparison of Freundlich Lead Adsorption onto Soil Types A and B in the Presence of EDTA

EDTA Concentration (moles/L)	Soil Type A		Soil Type B	
	1/n	<i>K_N</i>	1/n	<i>K_N</i>
0.00	0.71	4760	1.39	2.10
0.01	1.05	4.69	1.21	0.99
0.05	1.10	3.30	1.16	1.02
0.10	0.93	6.29	1.11	1.05

much higher silt/clay content for soil A as compared with a higher sand content for Soil B. Previous studies have indicated that heavy metals are preferentially bound to clays and humic materials [9].

ACKNOWLEDGMENTS

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NOMENCLATURE

- b* = Constant related to the net enthalpy of adsorption, used in the Langmuir isotherm model
- C* = Measure of solute (heavy metal) concentration in solution at equilibrium, (mg/L)
- EDTA = Ethylenediaminetetraacetic acid
- k* = Linear adsorption coefficient, (L/kg)
- K_N* = Empirical constant in the Freundlich isotherm model
- 1/n = Exponent in the Freundlich isotherm model
- NTA = Nitrilotriacetic acid
- pH = -log [H⁺]
- q_{e,0}* = Empirical constant used in the linear adsorption isotherm model, corresponding to the amount adsorbed with no addition of soil (i.e., an extrapolation form the *q_e* versus *C* plot)
- Q^o* = Amount of solute adsorbed per unit weight of soil in forming a complete monolayer on the surface of the soil, (mg/kg)

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Electrokinetic Removal of Selected Heavy Metals from Soil

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The electrokinetic process is an emerging technology for in situ soil decontamination, in which chemical species, both ionic and nonionic are transported to an electrode site in soil. These products are subsequently removed from the ground via collection systems engineered for each specific application. Electrokinetics refer to movement of water, ions and charged particles relative to one another under the action of an applied direct current electric field. In a porous compact matrix of surface charged particles such as soil, the ion containing pore fluid may be made to flow to collection sites under the applied field.

The work presented here describes part of the effort undertaken to investigate electrokinetically enhanced transport of soil contaminants in synthetic systems.

The results of the laboratory study presented here indicate that electrokinetic enhancement of contaminant transport in soils is a viable technology; development of this technology for wide range of applications hinges upon better understanding of the transient chemical and physical processes during application of current through soil/contaminant systems.

INTRODUCTION

Methods for cleaning up hazardous waste sites have changed since 1980 when the Comprehensive Environmental Response, Compensation and Liability Act, (CERCLA) or Superfund, was enacted. Early remedial actions for contaminated soils consisted primarily of excavation and removal of the contaminated soil from the site and disposal at a landfill. More emphasis is now placed on *in situ* treatment of soil. Electrokinetic decontamination is perhaps one of the most promising *in situ* soil decontamination process capable of removing heavy metals and organic contaminants from soil feasibly.

Electrokinetic decontamination invokes three electrokinetic processes: electroosmosis, electrophoresis, and electrolytic mi-

gration of ionic and polar species. Electroosmosis produces a rapid flow of water in low permeability soils and probably contributes significantly to the decontamination process in clay soils. Electrophoresis is the migration of charged colloids in soil-liquid mixture. In a compact system electrophoresis should be of less importance since the solid phase is restrained from movement. In some cases, however, electrophoresis may play a role in decontamination if the migrating colloids have the chemical species of interest adsorbed on them. During application of electricity to soil, water at the electrode sites as well as in the soil pores undergoes electrolysis, dissociating into its components, H^+ and OH^- . Electrolytic migration is the migration of ionic species present in the pore fluid as well as the migration of H^+ (produced at anode) and OH^- (produced at cathode) toward the opposite electrode. This migration is re-

sponsible for conducting the current in a soil-water system. As ions migrate toward an electrode, they can drag layers of water molecules, which may be of significant quantity if the ionic concentration of water content is high. Other reactions inherent to electrokinetics are ionic diffusion, and electrochemical reactions at the electrode sites. These reactions may or may not play significant roles in decontamination depending on the specific field process implemented and process control.

One of the important aspects of electrokinetics in soil-water systems is the transient migration of an acid front from the anode site to the cathode site during treatment [1, 2, 3]. When water decomposes, it is reduced to hydrogen gas at the cathode and oxidized to oxygen gas at the anode. This results in progressive reduction of pH at the anode site, and increase of pH at the cathode site. Subsequently the hydrogen ions produced at the anode migrate toward the cathode whereas the hydroxide ions produced at the cathode migrate toward the anode. Since the ionic velocity of the hydrogen ion is higher than that of the hydroxide ion, the H^+ would move faster into the soil. Sundberg [4] reports the relative mobility of H^+ as 318.0 versus 17.4 for OH^- . This movement would further be enhanced by the electroosmotic flow of water toward the cathode. Hydrogen ion will exchange with metal ions held on clay surfaces. In addition low pH condition is favorable for the dissolution of metal complexes and precipitates. Therefore, acid front migration is beneficial for metal extraction from soils, provided that soil's natural buffering capacity is sufficiently low. The transient and spatial variation of pH has further implications that aid in metal extraction. Soil surface properties such as cation exchange capacity, ion (cation and anion) adsorption capacity, and magnitude of surface potential and its sign are pH dependent. Furthermore, speciation and solubility of the contaminants are often pH dependent. The distribution of these contaminants would be transient and spatially varied with pH. In addition to the transient nature of pH, the soil redox potential would vary spatially in time during electrokinetic treatment. The pH-redox conditions at a point at any time during the treatment would determine the solubility and speciation of most heavy metal constituents. These conditions may limit or enhance the movement of the metals to an electrode site.

Extraction of contaminants by electrokinetic method is based on the assumption that the contaminant is in liquid phase in the soil pores. Sufficient flux of water produced by electroosmosis should be able to move non-ionic as well as ionic species through soil toward the cathode. This is perhaps best achieved when the state of the material (dissolved, suspended, emulsified, etc.) is suitable for the flowing water to carry it through the tight pores of soil without causing an immovable plug of concentrated material to accumulate at some distance from the anode, which would also restrict the flow of water. Polar organic molecules should orient themselves in the direction of the electric field, similar to water molecules, and move toward one of the electrode sites depending on their polarity, mobility and the surface charge characteristics of the soil medium. Removal of cationic species would be enhanced with the combined effect of electroosmotic flow of water and the electrolytic migration of the cation toward the cathode electrode. It is yet unclear the relative magnitude of contribution of either process (electroosmosis and electrolytic migration) to decontamination under a given set of initial and boundary conditions. However, recent findings indicate that at low concentrations of cations, electroosmotic water flow may contribute a significant percentage, if not all, to the overall decontamination process [5]. At high concentrations of the ionic species, electrolytic migration, intensity of electrochemical reactions, auxiliary water movement by hydraulic drag exerted on the hydrated ions (cations and anions) may play more important roles than electroosmosis in the decontamination process.

Earlier experimental observations by others [6, 7] also support the conclusion stated above. These investigations had shown significantly higher current efficiencies (volume of flow

per quantity of electricity) for low ionic concentrations or undissociated organic compounds in the pore fluid than those with high ionic concentrations in the pore fluid. Others [8] have argued that current efficiencies increase with increased ionic concentration in clay suspensions. This is a valid argument for colloidal suspensions in which true electroosmotic flow is probably not the predominant mechanism of water transport, but is the hydraulic drag exerted on the migrating ions. On the basis of the Donnan theory, a high water to cation concentration ratio promotes high current efficiency. Therefore in slurried systems, increased transport of water with increased cation concentration should hold true provided that the water concentration remains constant. In a compact system of soil, the rate of frictional dragging of water by ionic species through the pores is limited by the size of the pores and the pore throats. Therefore the ions may move as fast as they would in a loose suspension, however water will not. Under these conditions, increased ionic concentration at constant water content should decrease current efficiency according to the Donnan concept and observations made by others [7] and investigators of the work presented here.

BACKGROUND

Historical Development of Electrokinetic Processes in Soils

Electrokinetic phenomenon was first discovered by Reuss in 1808. The phenomenon was first treated analytically by Helmholtz in 1879, which later was modified by Pellat in 1904 and Smoluchowski in 1921. This theory is widely known as Helmholtz-Smoluchowski theory which relates electroosmotic velocity of a fluid of certain viscosity and di-electric constant, through a surface charged porous medium of zeta potential, ζ , under an electric gradient. The theoretical computation of electroosmotic water transport, by this theory does not always agree well with experimental observations. The zeta potential term in the H-S theory varies with pH and ionic concentration of the pore fluid, which is not a constant during electrokinetic treatment. Similarly, electric gradient is not constant in time and space due to the changing resistivity and oxidation/reduction state of the soil.

A notable approach to electrokinetic process in porous medium was made by Spiegler [9]. He considered the interactions of the mobile components of soil (water and ions) on each other and the frictional interactions of these components with the pore walls. The true electroosmotic flow was expressed as the difference between the measured water transport and the ion hydration in moles per Faraday. This quantity was suggested to be directly proportional to concentration of free water in the soil pores and indirectly proportional to the concentration of mobile counterions in moles per volume. This suggests the phenomenon of water transport in the opposite direction of electroosmotic flux by the electrolytic migration of the anions. Therefore, at any time during electrokinetic treatment if the concentration of anionic species in the free water exceeds the cationic species, the opposite flow may retard the net flow toward the cathode.

Gray and Mitchell [7] showed experimentally that the electroosmotic flow increases with increasing water content of most soils, however decreases with increasing electrolyte concentration of the pore fluid. This electrolyte concentration effect is more evident in clays with high anion retention capacity, such as kaolinite, as opposed to montmorillonite [10]. Therefore high electroosmotic flows are observed in kaolinite than montmorillonite type of clays at the same concentration of dilute solutions of electrolytes. This is consistent with the prediction of electroosmotic water transport according to Donnan concept.

Khan [5] proposed a modified theory of electroosmotic flow through soil. In this theory the true electroosmotic flow is directly proportional to the current carried by the surface of the charged soil constituents of soil. The slipping plane potential (zeta potential) used in Helmholtz-Smoluchowski theory of electroosmotic flow is replaced by a constant surface potential which is invariable with electrolyte concentration. Hence, true electroosmotic flow becomes independent of electrolyte concentration in the pore fluid. The measured values agree well with the predicted flow using this modified theory. It also agrees with Speigler's [10] formulation and much earlier observations of Napier in 1846 [12] who stated that "... the measurable endosmose (electroosmosis) seems to be greatest when the current has greatest difficulty to pass through, and when the decomposition (of water) was least." This follows that the true electroosmotic flow is large when ratio of the surface current to the electrolytic current (carried by the ions in the pore fluid) is large due to reduced concentration of ions in the pore fluid.

Application of Electrokinetics to Soil Decontamination

Electrokinetics have been used for dewatering of soils and sludges since the first recorded use in the field by Casagrande in 1939 [12]. Work and subsequent research in electrokinetic decontamination of soils have been accelerated in recent years, probably after the report of the detection of high concentrations of metals and organics in electroosmotically drained water of a dredged sludge in the field by Segall and co-workers in 1980 [13]. Other field work [14, 15] has been conducted since then with reasonable success of heavy metal transport.

Hamnett [16] performed laboratory studies on electrically induced movement of ions in sand. In evaluating the electrolytic migration of ions of different salts, he found that smaller ions (i.e., Na) were more mobile than larger ions (i.e., K, Ca, Ni). Acar et al. [17] and Hamed et al. [18] showed that the migration of an acid front from the anode toward the cathode is significant in the removal of heavy metals from clay soils. Shapiro and co-workers [3] developed a model for electroosmosis to predict transient behavior of concentration profiles for chemical species in solution. The model agreed well with experimental results of acetic acid removal from soil via electrokinetics.

A simple prediction method was suggested by Khan [5] recently. The theoretical approach developed for electroosmotic flow was used to predict the contaminant removal from soil when the contaminants are either present at low concentrations in the soil pores or they are not adsorbed onto the charged surfaces, so that the true electroosmotic flow is the dominant mechanism for their migration. Tracer experiments in kaolinite clay utilizing O-Nitrophenol and zinc as representative contaminants were conducted. O-Nitrophenol represents a poorly adsorbed organic compound, the adsorption of which was measured on the order of 0.01 mg/g of soil. The zinc concentration used was 325 mg/kg of dry soil which was slightly over than the typical maximum concentration of naturally occurring zinc (10-300 mg/kg) in soils. There was good agreement between the measured removal of the contaminant and the predicted removal using electroosmotic flux of water based on clay surface current.

INVESTIGATION

Experimental Procedures

An extensive laboratory program was undertaken to investigate the feasibility of electrokinetic treatment of clay mixtures containing heavy metals. The test matrices were prepared in the laboratory by compressing slurries of clay to compact saturated soil samples. Each clay slurry was mixed with solution

of one heavy metal salt of a predetermined concentration. The mixing water of the slurries were also changed as distilled water, a solution of a humus product representing humic acids in natural soils, and water with dissolved salts representing the ionic constituents of a selected groundwater type. Each specimen type (clay, pore solution and metal type) was prepared in triplicate and tested under the same conditions, but with variable duration of treatment for some of triplicate sets. In the overall testing program, 11 different metals (As, Cd, Co, Cr, Cs, Hg, Ni, Pb, Sr, U, Zn) were used. The initial mixing concentrations of some of these metals were varied from a typical low to a high value occurring in field situations. In this paper, results of electrokinetic treatment and implications of a few of the clay + pore water + metal combinations are presented. The metals used in these combinations were Cd, Co, Ni and Sr.

Materials

The clays used in preparing the soil matrices were kaolinite (Georgia kaolinite) and Na-montmorillonite (bentonite), both obtained commercially. The sand specimens were prepared with washed New Jersey beach sand passing No. 40 sieve and retained on No. 100 sieve. This variation in soil mineral matrix was intended to investigate the process in so assumed difficult situations of remediation when the ionic species are strongly held on the clay surface (Na-montmorillonite case), or when the electroosmotic flow efficiency might be reduced due to reduced surface charge density (sand case). The sand matrix was prepared with the clean beach sand mixed homogeneously with 10% Na-montmorillonite by dry weight.

The pore solutions were distilled water, humic solution and simulated groundwater. The humic solution was prepared by dissolving a commercially obtained humus product in distilled water at a concentration of 900 ppm. The organic carbon content of this stock solution was 257 as measured in mg C/l. This corresponded to DOC values typically measured in groundwaters associated with very high organic carbon fields, such as oil fields. The pH of this solution was 9.4. The simulated groundwater was prepared following an approximate formula of the groundwater salt constituents typically found in the Jefferson County of Idaho State. The pH of groundwater sampled in that region was measured at 8.2, and contained a substantial amount of (212 ppm) bicarbonate. The simulated groundwater did not contain this component. Its pH was measured as 7.9.

The salts used in preparing solutions of the 4 metals and the metal concentration of each resulting solution as well as the resulting concentration of the metal in soil and the soil pH prior to electrokinetic treatment are given in Table 1. Some of these metal solutions were prepared at so called "high" and "low" concentrations to represent variable degree of contamination of the soil matrix. In general the pHs of the mixtures were moderately acidic or near neutral. In most cases the pH was reduced with the addition of the metal salt, probably because they all were salts of strong acids.

Procedures

The slurries would be mixed at 100% water content of the kaolinite clay, 50% water content of the sand mixture, and 200-300% water content of Na-montmorillonite clay, all by dry weight of the solid components. The mixing would be done in large batches (2-3 gallons) with a tall hand held mixer. Then the slurry would be poured into individual compression units referred to as "consolidometers." The operation of these units are presented elsewhere [5]. The main features of the consolidometers are that they are capable of applying some increments of sustained stress (pneumatically) while allowing for

Table 1 Some Properties of the Materials Used in Preparing Specimens

Sample Code*	Metal	Salt Formula	Solution		Soil		Initial Soil pH
			Concentration (mg/l) High	Low	Concentration (mg/kg) High	Low	
KS	Blank	—	—	—	—	—	4.36
	Cd	CdCl ₂ ·(2.5)H ₂ O	1000	40	666	40	4.15
	Co	CoCl ₂ ·6H ₂ O	1000	—	677	—	3.33
	Ni	Ni(NO ₃) ₂ ·H ₂ O	1000	—	395	—	3.40
	Sr	SrCl ₂ ·6H ₂ O	1000	—	686	—	4.31
KH	Blank	—	—	—	—	—	6.26
	Cd	—	1000	—	748	—	5.98
	Co	(same as above)	1000	—	599	—	5.73
	Ni	—	1000	—	701	—	6.26
	Sr	—	971	—	N/A	—	5.96
KG	Blank	—	—	—	—	—	5.37
	Cd	—	1000	—	630	—	5.38
	Co	(same as above)	1000	—	550	—	5.49
	Ni	—	1000	—	1084	—	3.90
	Sr	—	971	—	N/A	—	5.97
MS	Blank	—	—	—	—	—	7.94
	Cd	—	1000	N/A	4972	882	6.37
	Co	(same as above)	1000	—	8603	—	6.13
	Ni	—	1000	—	5617	—	6.76
	Sr	—	971	—	4432	—	7.83
SS	Blank	—	—	—	—	—	7.34
	Cd	—	1000	N/A	N/A	N/A	5.46
	Co	(same as above)	1000	—	1020	—	6.18
	Ni	—	1000	—	598	—	7.41
	Sr	—	971	—	463	—	8.20

*KS: Kaolinite/distilled water
 KH: Kaolinite/Humic solution
 KG: Kaolinite/Groundwater

MS: Na-Montmorillonite/distilled water
 SS: Sand + 10% Na-Montm./distilled water

the excess fluid to drain out slowly. This procedure creates, homogeneous, near saturated soil matrices compacted to a constant density and pressure. The most beneficial aspect of these custom manufactured units is that at the end of the consolidation process, the densified soil sample is packed into a cylindrical soil chamber (3.556 cm ID and 7.62 cm long) which can be detached from the unit and installed into the electrokinetic cell used in this investigation. Therefore the resulting soil specimen is not disturbed by handling such as trimming and placement.

All the specimens were consolidated to 200 kPa pressure. Although there is evidence, from this work and others [22] that, electroosmotic flow increases with consolidation pressure in clay soils, it is not well known to what extent the increased flow contributes to decontamination when the contaminant migration is not governed by electroosmosis. The average initial densities and water contents of the five artificial soil types are given in Table 2.

At the completion of each consolidation period, the tube containing the packed soil would be removed, the top extruding portion trimmed and stored for quantitative chemical and water content analysis. Samples of the waters extracted during consolidation were also taken for chemical analysis to assess the degree of metal retention by clays. The approximate period of consolidation to 200 kPa pressure was around 24 hours for kaolinite and it was around 7 days for Na-montmorillonite clays slurries. This period was much less for the sand + bentonite specimens, but pressure increment periods were maintained similar to that of kaolinite for consistency. When the soil cylinder was removed from the consolidometer, weighted and sampled, it would be ready for mounting on the electrokinetic apparatus.

The details of the electrokinetic apparatus used in this study are also provided elsewhere [5]. It should be noted that there

is no standard apparatus for measuring electrokinetic water flow in soils. The ones that are used in similar work elsewhere have been shown to produce consistent results. The equipment used in this particular program was developed with attention given to a few concerns. These were addressed by providing larger electrode surfaces than soil surface to achieve low current density, by isolating the electrodes from soil surfaces to minimize electrode reactions at these boundaries, and by providing convenient ports for gas expulsion from the electrode sites and also extracting inflow (anode site) and outflow (cathode site) water samples for analysis. The main features of these units are: the electrodes reside in water tight chambers which are connected to measuring burettes at one end, and to the soil specimen cylinder at the other end. The soil specimen is separated from these water filled chambers by carborandum po-

Table 2 Average water content and density of specimens before and after electrokinetic treatment

Sample Code	Initial		Final	
	W %	density (g/cm ³)	W %	density (g/cm ³)
KS	47.25	1.64	56.19	1.62
KH	51.35	1.66	54	1.54
KG	32.8	1.83	39.5	1.73
MS	271.8	1.14	321.62	1.03
SS	51.25	1.67	52.95	1.66

KS: Kaolinite-distilled water
 KH: Kaolinite-humic solution
 KG: Kaolinite-ground water
 MS: Montmorillonite-distilled water
 SS: Sand & 10% Montmorillonite-distilled water

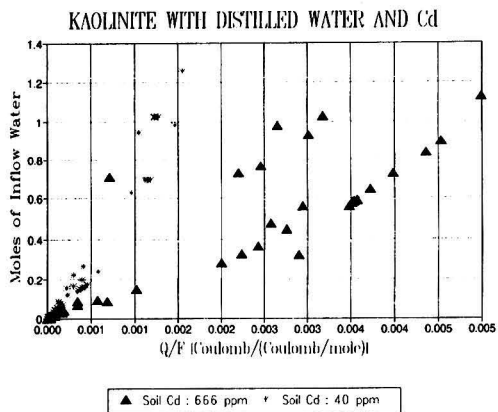


FIGURE 1. Variation of quantity of water flow versus number of moles of electrons transmitted in kaolinite with distilled water and cadmium.

rous stones. The units can be operated under constant potential or constant current. The time dependent water movement through the soil is detected by monitoring the water levels in the inflow (anode side) and outflow (cathode side) tubes on individual control panels. These panels are also each equipped with a pressure regulator and gauge for hydraulic potential application capability. The control panels also carry small pumps to drain the electrode chamber periodically as necessary in order to remove the extracted material and alleviate concentration polarization.

The tests, results of which are reported here were conducted under a constant potential of 30 VDC across electrodes. The voltage in soil and the current generated were measured simultaneously with the flow measurements. The tests were continued for at least 24 hours. For a number of randomly selected combinations of soil, pore fluid and metal, the termination times were varied between the triplicate samples from 24 hours to up to 50 hours. For a number of extended hours of treatment, the electrode chambers (both anode and cathode) were

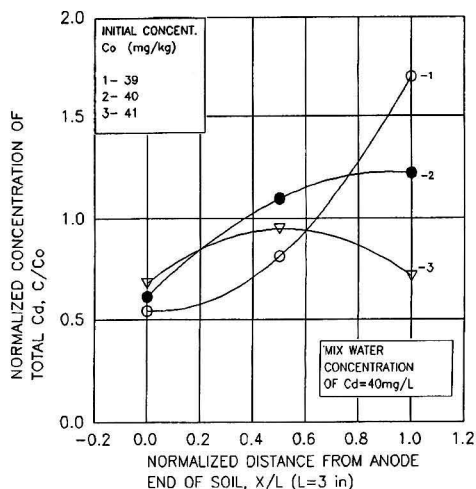


FIGURE 3. Normalized concentration variation of Cd (low concentration) from the anode to the cathode end of 3 replicate specimens of kaolinite with distilled water.

drained at around 24 hours and refilled with the appropriate pore water used in the soil specimen. This was done to alleviate concentration polarization and the high pH gradients created between the chambers which was thought to reduce water flow rate originally. However, this practice did not prove to be effective for increased contaminant removal or water flow rate, therefore it was abandoned in the later tests.

At the termination of each experiment, the chamber water would be collected. The cathode chamber water was acidified to solubilize the metal precipitates created at the high pH environment in that chamber. These water samples were analyzed for the particular metal extracted and their pHs were measured. The cathode water pHs ranged from around 10 to 12, whereas the anode water pHs ranged from 2 to 3 in general. The soil specimen would then be extracted, pH measurements taken at the anode end, center and the cathode end. Specimens from each one of these locations were collected for chemical analysis of the particular metal aimed for extraction.

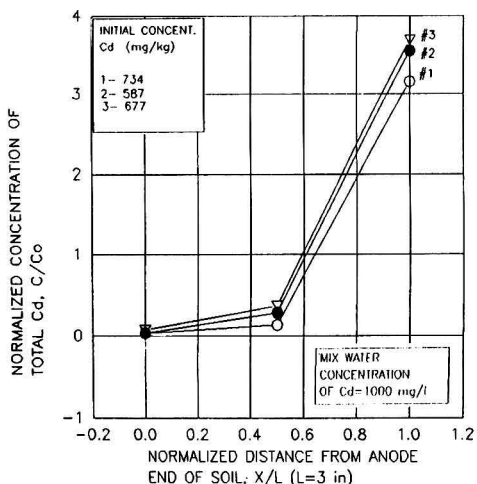


FIGURE 2. Normalized concentration variation of Cd (high concentration) from the anode to the cathode end of 3 replicate specimens of kaolinite with distilled water.

RESULTS

The analysis of available data showed metal migration in all soil specimens. Considering the metal concentrations reached in the first half of the soil specimen (anode half) or the lowest concentration of a particular metal achieved at one of the three locations (anode end, center, cathode end) of the soil cylinder, the metal removal success ranged between 85–95% (based on original concentration). These values were mostly achieved with specimens containing the higher concentration of a particular metal. The slight variations in these removal percentages appeared to depend on soil matrix, the metal and pore fluid type. It should be noted here that, the concentration profiles of metals across the soil specimens were generated by sampling only three points along each specimen. Therefore the actual concentration profile at the time of sampling may not be well represented by the linear or best fit distributions assumed between the consecutive points. Therefore, it is not possible to predict degree of removal of the contaminant from the areas under the concentration curves, neither arrive at an accurate mass-balance prediction. Nevertheless, the data presented are consistent and show a clear trend of metal migration toward an electrode site in each case.

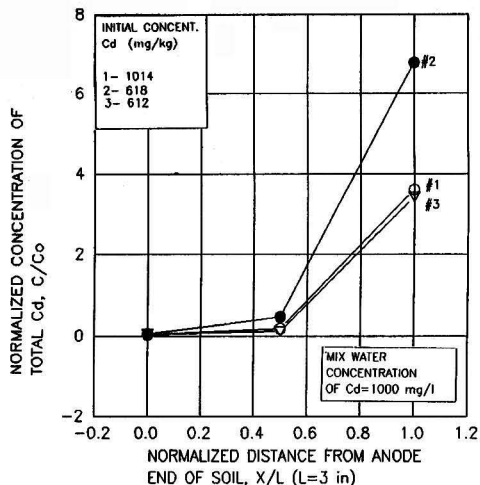


FIGURE 4. Normalized concentration variation of Cd (high concentration) from the anode to the cathode end of 3 replicate specimens of kaolinite with humic solution.

The lower concentration metal mixed soils did not show as high percentages of removal for the same durations of treatment. Figure 1 shows the correlation between moles of inflow water versus the quantity of electricity (moles of electrons) passed through two types of kaolinite soil specimens—each in triplicate—with distilled water and varying initial concentrations of cadmium measured in milligrams per kilogram of dry soil (Table 1). As observed, the low concentration Cd specimens exhibit larger influx of water than the high Cd concentration specimen for the same level of electricity. The average removal of Cd in the first half of soil cylinder was computed as 16.5% for low concentration case, whereas this percentage was 84 for the high Cd concentration case. Figures 2 and 3 illustrate the concentration profiles of Cd across the soil specimens based on the quantitative measurements made at three locations in the specimen. At low concentration of the metal, the current carried by the clay surface may constitute a larger portion of the total current and result in larger net flow of water in the cathode direction, or electroosmosis, as observed by Napier in 1846. At high concentrations of the metal the current is easier to pass through, because the bulk of it would be carried through the pore space. The quantity of true electroosmotic flow may remain the same, however the flow would probably be counteracted by the movement of a larger concentration of anions that drag water molecules along. The anion retention of the clay then plays an important role in the development of a net water flow to the cathode.

The other results pertaining to Cd removal in kaolinite in the presence of pore fluids other than distilled water are presented in Figures 4 and 5, for the humic solution and simulated groundwater, respectively. As observed, the initial retention of Cd in kaolinite does not change significantly when the pore water changes from distilled water. The removal trends, however, changes slightly. The low concentrations of the metal in the first half of the cell are repeated, but at the cathode end of the soil the concentrations are increased compared to that of the distilled water specimens. The average pHs measured at the cathode ends of these specimens were determined as 5.3, 9.0 and 8.1 for the distilled water, humic solution and groundwater specimens, respectively. The accumulation of a metal product may be due to two conditions: one is that the time rate of migration of a metal may be higher than its rate of release into the electrode chamber, and the other is that in-

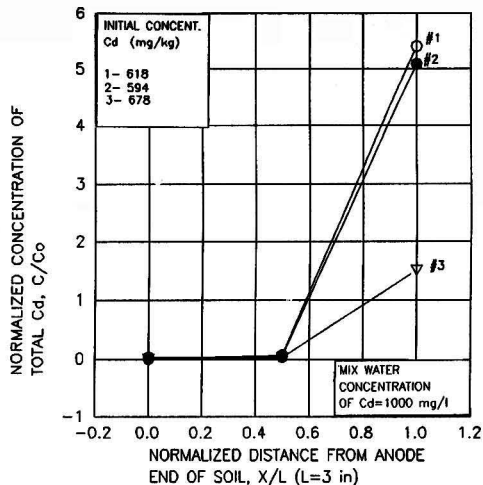


FIGURE 5. Normalized concentration variation of Cd (high concentration) from the anode to the cathode end of 3 replicate specimens of kaolinite with simulated groundwater.

creased pH environment may favor non-ionic or anionic species of the metal which would then precipitate or tend to move in the opposite direction of the flow. The former condition may be due to a number of reasons such as concentration polarization in the electrode chamber, ionic diffusion due to the large pH gradient at the interface between the soil and the cathode chamber, increased level of electrochemical reactions close to the boundary which may result in retardation of the flux, or physical entrapment due to reduced permeability at the boundary. The increased pH in the latter two cases of Cd with humic solution and groundwater might have contributed to accumulation of the metal at the cathode end. This is in agreement with the distribution of hydrolysis products of Cd⁺ with pH. Until around pH 8, Cd remains in ionic form with +2 charge. Above this value it starts forming complex species which are either charged positively or negatively or neutral. The tendency of each one of these products and their abun-

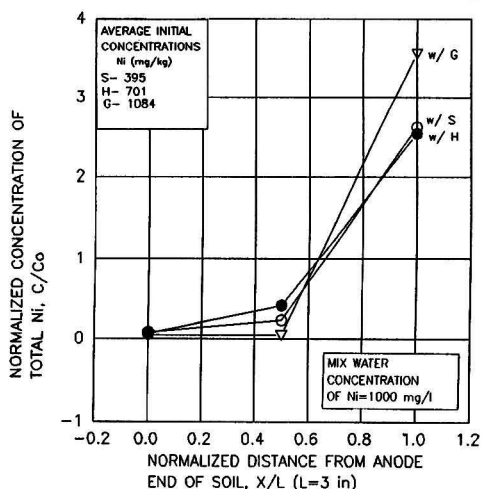


FIGURE 6. Average normalized concentration variation of Ni from anode to cathode end of specimens of kaolinite with distilled water, humic solution and simulated groundwater.

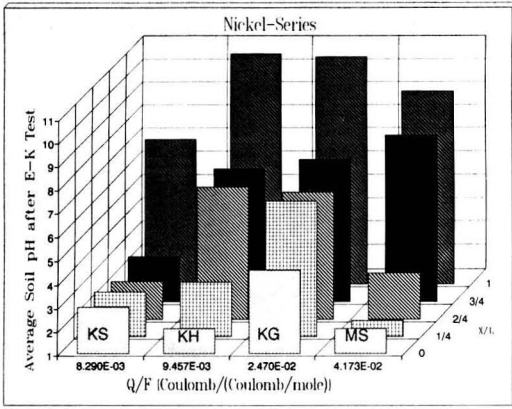


FIGURE 7. Average pH distribution from anode to cathode end in 3 duplicate specimens of four clay types with nickel at the end of electrokinetic treatment.

(KS: kaolinite/distilled water, KH: kaolinite/humic sol. KG: kaolinite/groundwater, MS: Na-montmorillonite/dist. water)

dance will control the removal rate for some time until the acid front reaches the cathode end. Even so, the removal rate into the electrode chamber may still be affected significantly by the boundary conditions discussed above. Another important aspect that needs to be addressed is the increased adsorption and cation exchange capacity of the clay at high pH environments. Therefore, the accumulation of the metal at the cathode end would be favored by the changing surface characteristic of the soil at the interface with the cathode chamber where the pH is typically measured above 10.

A similar trend was observed with nickel mixed at high concentration into kaolinite. Figure 6 shows the average of the concentration profiles for high concentration nickel in kaolinite clay with the three different pore fluids. Once again the metal removal in the anode half of the soil is moderately high, on the order of 50% for distilled water and humic solution specimens and it is about 80% for the groundwater specimens. The average pH distribution at the completion of treatment from anode ($x/L = 0$) to cathode ($x/L = 1$) end of four Ni

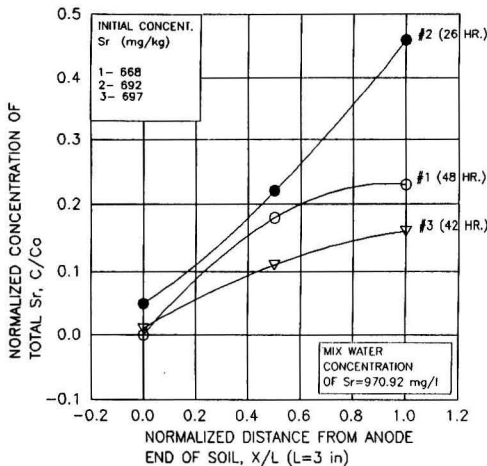


FIGURE 8. Normalized concentration variation of Sr (high concentration) from the anode to the cathode end of 3 replicate specimens of kaolinite with distilled water.

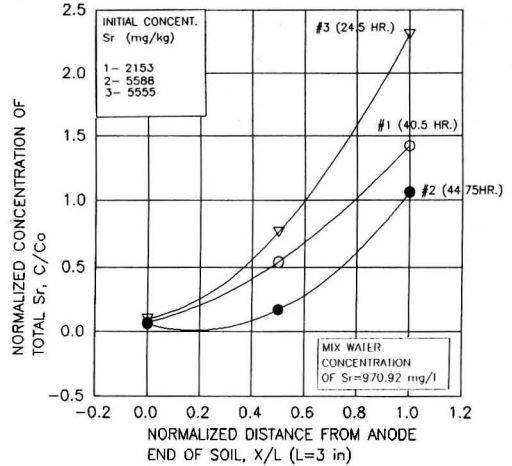


FIGURE 9. Normalized concentration variation of Sr (high concentration) from the anode to the cathode end of 3 replicate specimens of Na-montmorillonite with distilled water.

carrying clay soils are presented in Figure 7. As expected, the smallest quantity of electricity corresponds to the distilled water kaolinite specimens, while the highest value corresponds to Na-montmorillonite specimens. The hydrolysis products of Ni are also complex ions of positive or negative charge or solid, which start to form above pH 7. Observing the chart in Figure 7, one can predict the types of Ni complex species that may occur along the specimen.

Strontium remains a divalent ion for a large range of pH values. Figure 8 illustrates successful removal of Sr from distilled water kaolinite specimens. The progressive reduction of the element at the cathode end also shows the transient nature of the process. Similar trends were observed with Sr in Na-montmorillonite and sand + montmorillonite mixture with distilled water. These are presented in Figures 9 and 10, respectively. The average pH distributions are given in Figure 11, where the cathode end pHs are high for two of the soil types. Considering the Na-montmorillonite and sand + ben-

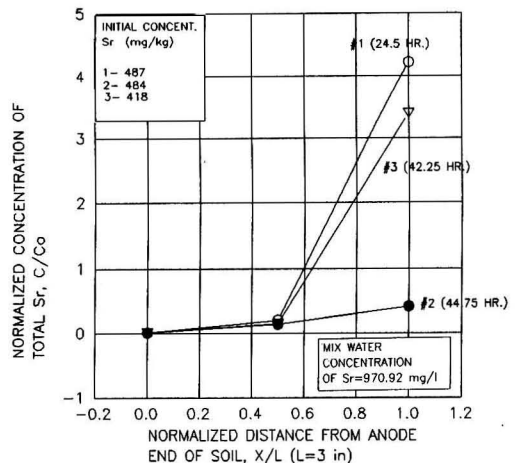


FIGURE 10. Normalized concentration variation of Sr (high concentration) from the anode to the cathode end of 3 replicate specimens of sand + 10% Na-montmorillonite with distilled water.

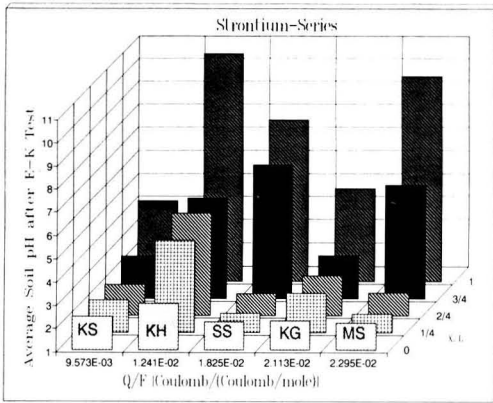


FIGURE 11. Average pH distribution from anode to cathode end in 3 duplicate specimens of five soil types with strontium at the end of electrokinetic treatment.

(KS: kaolinite/distilled water, KH: kaolinite/humic sol. KG: kaolinite/groundwater, MS: Na-montmorillonite/dist. water, SS: clayey sand/distilled water)

tonite specimens, the cathode pH should not effect strontium since it will remain a divalent ion even at high pHs. However, there is accumulation of the metal at the cathode end which appears to deplete in time, as shown in Figures 9 and 10. Once again, this delayed flux of the metal into the cathode chamber may be due to a number of factors some of which are ionic diffusion, migration of counterions, or increased levels of electrochemical reactions at the increased concentrations of the metal and also the exchange potential of the soil.

Finally, the concentration profile of cobalt in distilled water kaolinite is presented in Figure 12. The pH distributions for the clay soils with Co are given in Figure 13. The average pH at the cathode end of the distilled water kaolinite specimen was over 9, which is within the range of pHs for complex ion formations of Co. Depending on the local concentration of Co^{+2} at this pH, the predominant species may either be a positively charged ion or an hydroxide salt, $Co(OH)_2$.

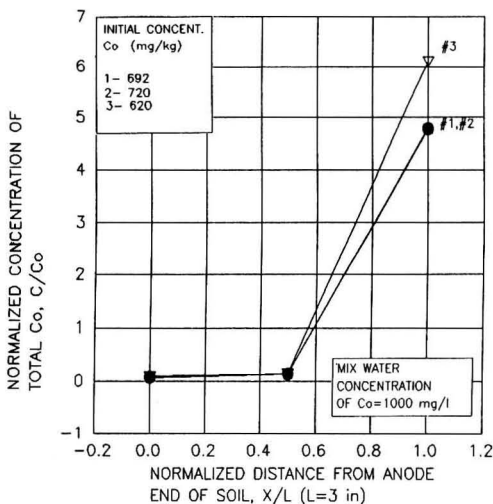


FIGURE 12. Normalized concentration variation of Co (high concentration) from the anode to the cathode end of 3 replicate specimens of kaolinite with distilled water.

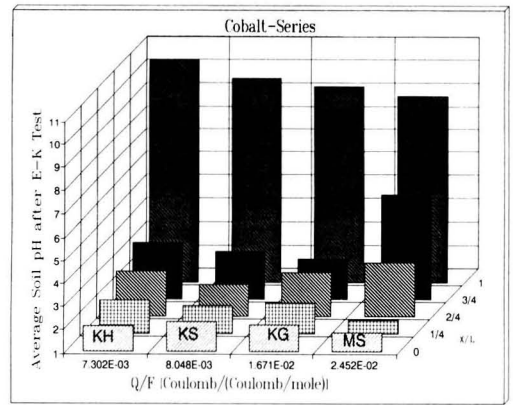


FIGURE 13. Average pH distribution from anode to cathode end in 3 duplicate specimens of four clay types with cobalt at the end of electrokinetic treatment.

(KS: kaolinite/distilled water, KH: kaolinite/humic sol. KG: kaolinite/groundwater, MS: Na-montmorillonite/dist. water)

Figure 14 presents the correlations between inflow quantity normalized by updated pore water volume, versus moles of electrons transferred for the three different soil types with distilled water. Each one of the soil samples contain one of the 4 metals, Sr, Ni, Co or Cd. The linear relationship is evident in each soil type, with kaolinite representing the most consistent behavior with a narrow span of variation. Sand + bentonite specimens have a larger span than that of kaolinite, whereas the montmorillonite relationship varies considerably. Flow through montmorillonite specimens appear to be more affected by the type of metal than it is for kaolinite specimens. At the top of the montmorillonite data span resides the flow data of Sr clay mixtures, then for Co mixtures and towards the bottom is the data for Ni mixtures. A trend is observed from the overall data, that is, for the same number of moles of electrons, the inflow to pore water volume ratio is highest for kaolinite and it is more or less independent of the type of the metal ion present in the pore fluid, when compared to other two soil types. It should be noted here that, this is valid for the four metals tested. The sand + montmorillonite trend is similar but slightly lower than that of kaolinite. Although montmorillonite appears to produce the lowest ratio, because of its large span,

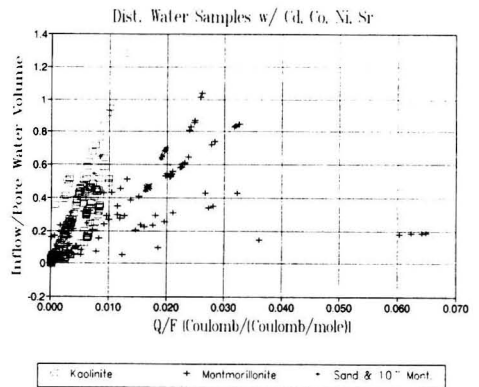


FIGURE 14. The variation of normalized cumulative inflow versus the number of moles of electrons transmitted in distilled water specimens of the three types of soils with Cd, Co, Ni or Sr.

Dist. Water in Kaolinite w/ Co, Ni, Sr, Cd

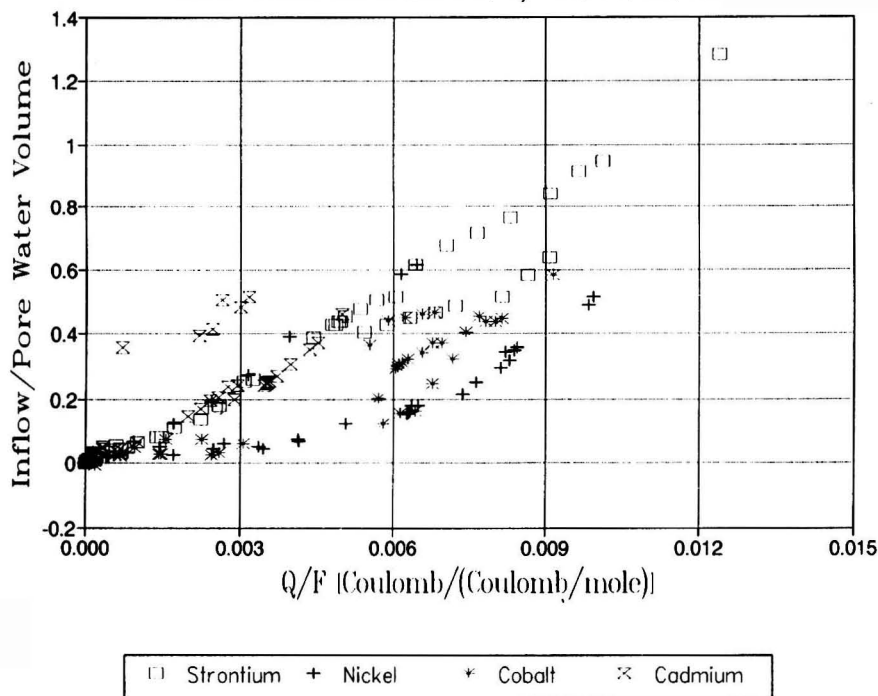


FIGURE 15. The variation of normalized cumulative inflow versus the number of moles of electrons transmitted in distilled water specimens of kaolinite with Cd, Co, Ni or Sr.

such a conclusion is not made at this time until further data is processed.

In Figure 15 normalized inflow versus moles of electrons is reproduced for kaolinite only. The slope of approximate straight line correlations change as the metal in the pore fluid varies. In general the trends are similar to those of metal + Na-montmorillonite mixtures shown in Figure 14. In this case, Sr and Cd specimen data coincide, exhibiting the largest flow per mole of electron value, whereas Ni shows the smallest value, among the four metal mixtures. The reduced flow may be due to the formation of complex species of ions produced as pH changes across a specimen. At times when there are predominantly negative complexes of a metal, these species may carry significant number of molecules of water as they migrate in the opposite direction of electroosmotic water flow, reducing the net flow towards cathode.

CONCLUSIONS

The main conclusion of this research has been that electrokinetics promises to be a viable technology to remove contaminants from soils. The interaction of various processes that take place simultaneously is yet to be understood to better predict the efficiency of the process in a variety of soil-contaminant situations. The results presented in this paper shed some light on the influence of electrochemistry and physicochemistry of the soil-contaminant system on the process. The transient acid front movement in soil from anode site to cathode, is beneficial for metal desorption and dissolution, which in turn contributes to the removal process. However, the transient pH condition cause formation of complex species of some metals which may hinder the process, or in some cases enhance it. Therefore pH control at both ends (anode and cathode)

should create suitable environments for the metal ions to remain in solution as single species, so that realistic predictions of rate of electrokinetic extraction can be made.

The following specific conclusions were obtained from this study:

1. Electroosmosis is probably the dominant mechanism of electrokinetic extraction of metal contaminants when they are present at low concentrations. At high concentrations of the metal, electrolytic migration of their ionic species plays a more important role than the electroosmotic transport.
2. The removal of the 4 metals tested in this study from a variety of soil types, including montmorillonite, kaolinite, clayey sand, clay with simulated groundwater and clay with humic acids was achieved at 85-95% of the original concentration, characterized as typical high concentration of these metals occurring in some common sites.
3. At low concentration of Cadmium, the flow efficiency was higher than the high concentration case of the metal. However, percent removal was 16.5 as opposed to 84 percent for the latter case.
4. Among the 3 soil types tested, kaolinite exhibited highest efficiency of electrokinetic water flow, followed by clayey sand. The lowest efficiency appeared to occur with Na-montmorillonite. Kaolinite exhibited consistent efficiency with little variation with respect to the metal ion type. Whereas, montmorillonite and clayey sand appeared to be more affected by the type of metal ion.

ACKNOWLEDGMENTS

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