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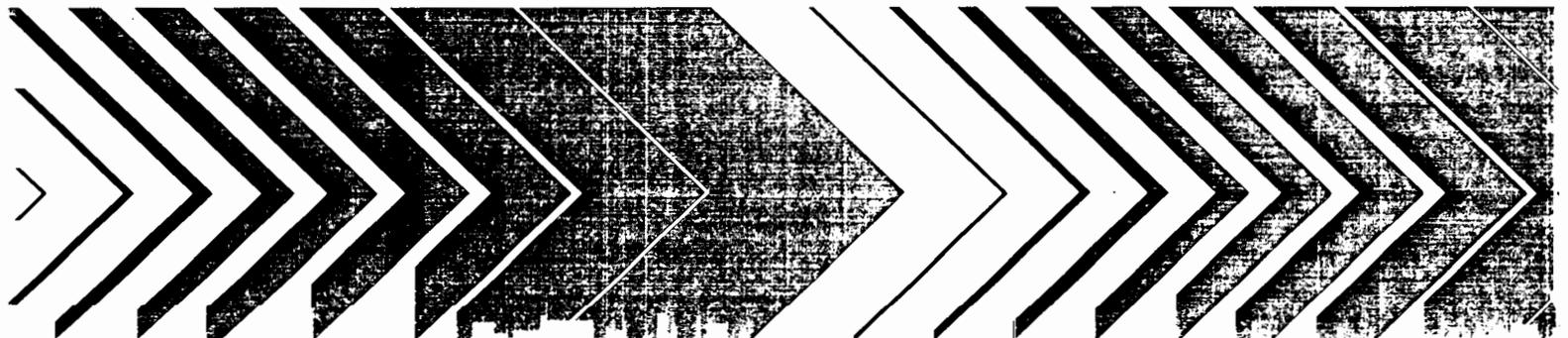
Research and Development

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# **Remedial Action, Treatment, and Disposal of Hazardous Waste**

**Proceedings of the  
Seventeenth Annual  
RREL Hazardous  
Waste Research  
Symposium**





REMEDIAL ACTION, TREATMENT, AND DISPOSAL  
OF HAZARDOUS WASTE

Proceedings of the Seventeenth Annual Hazardous Waste Research Symposium  
Cincinnati, OH, April 9-11, 1991

Sponsored by the U.S. EPA, Office of Research & Development  
Risk Reduction Engineering Laboratory  
Cincinnati, OH 45268

Coordinated by:

JACA Corp.  
Fort Washington, PA 19034

under subcontract to:

Science Applications  
International Corporation  
Cincinnati, OH 45203

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## NOTICE

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## FOREWORD

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

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

These Proceedings from the 1991 Symposium provide the results of projects recently completed by RREL and current information on projects presently underway. Those wishing additional information on these projects are urged to contact the author or the EPA Project Officer.

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

E. Timothy Oppelt, Director  
Risk Reduction Engineering Laboratory

## ABSTRACT

The Seventeenth Annual Research Symposium on Remedial Action, Treatment, and Disposal of Hazardous Waste was held in Cincinnati, Ohio, April 9-11, 1991. The purpose of this Symposium was to present the latest significant research findings from ongoing and recently completed projects funded by the Risk Reduction Engineering Laboratory (RREL).

These Proceedings are organized in three sections: Sessions A and B consist of paper presentations. Session C contains the poster abstracts. Subjects include remedial action treatment and control technologies for waste disposal, landfill liner and cover systems, underground storage tanks, and demonstration and development of innovative/alternative treatment technologies for hazardous waste. Alternative technology subjects include thermal destruction of hazardous wastes, field evaluations, existing treatment options, emerging treatment processes, waste minimization, and biosystems for hazardous waste destruction.

CONTENTS

SESSION A

	<u>Page</u>
Site Demonstration of Microfiltration Technology for Groundwater Contaminated with Metals John F. Martin, U.S. Environmental Protection Agency.....	1-4
Site Demonstration of the CF Systems Organic Extraction Process Laurel J. Staley, U.S. Environmental Protection Agency.....	5-18
Summary Results of the SITE Demonstration for the CHEMFIX Solidification/Stabilization Process Edwin F. Barth, U.S. Environmental Protection Agency.....	19-27
Soil Vapor Extraction: Air Permeability Testing and Estimation Methods Chi-Yuan Fan, U.S. Environmental Protection Agency.....	28-42
Underground Storage Tanks Containing Hazardous Chemicals Joseph Maresca, Vista Research, Inc.....	43-56
Subsurface Fate and Transport of Petroleum Hydrocarbons From Leaking Underground Storage Tanks: A Basis for Evaluating The Effectiveness of Corrective Actions Warren J. Lyman, Camp, Dresser & McKee.....	57-65
The Incineration of Lead-Contaminated Soil Related to the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) (Superfund) Howard O. Wall, U.S. Environmental Protection Agency.....	66-78
Full-Scale POHC Incinerability Ranking and Surrogate Testing Andrew Trenholm, Midwest Research Institute.....	79-88
EPA's Mobile Volume Reduction Unit for Soil Washing Hugh Masters, U.S. Environmental Protection Agency.....	89-104
Guidance for Treatability Testing Under CERCLA: An Update David Smith, U.S. Environmental Protection Agency.....	105-118
S.I.T.E. Demonstration of A Soil Washing System by Biotrol Inc., at a Wood Preserving Site in New Brighton, Minnesota Mary K. Stinson, U.S. Environmental Protection Agency.....	119-130
Background Information on Clean Products Research and Implementation Marjorie A. Franklin, Franklin Associates, Ltd.....	131-145
Industrial Pollution Prevention Strategy: Research Priorities and Opportunities for the 1990's Ivars J. Licis, U.S. Environmental Protection Agency.....	146-161

SESSION A (Continued)

	<u>Page</u>
The Evaluation of an Advanced Reverse Osmosis System at the Sunnyvale, California Hewlett-Packard Facility Lisa M. Brown, U.S. Environmental Protection Agency.....	162-171
The Behavior of Trace Metals in Rotary Kiln Incineration: Results of Incineration Research Facility Studies D.J. Fournier, Jr., Acurex Corporation.....	172-189
Soil Heating Technologies for In Situ Treatment: A Review Janet M. Houthoofd, U.S. Environmental Protection Agency.....	190-203
The United States Environmental Protection Agency Municipal Waste Combustion Residue Solidification/Stabilization Program Carlton C. Wiles, U.S. Environmental Protection Agency.....	204-224
Weathering of Selected Degradable Plastic Materials Under Outdoor and Laboratory Exposure Conditions Anthony L. Andrady, Research Triangle Institute.....	225-237
Pollution Prevention Research Within the Federal Community James S. Bridges, U.S. Environmental Protection Agency.....	238-257
Toxic Substance Reduction for Narrow-Web Flexographic Printers Paul M. Randall, U.S. Environmental Protection Agency.....	258-286

SESSION B

	<u>Page</u>
The Treatability of Urban Stormwater Toxicants Patricia F. Barron, Law Engineering.....	287-308
Report on Enhancing Effects of Low Frequency Vibration in Soil Washing Malvina Wilkens, U.S. Environmental Protection Agency.....	309-328
Vacuum-Assisted Steam Stripping to Remove Pollutants from Contaminated Soil: A Laboratory Study Arthur E. Lord, Jr., Drexel University.....	329-352
Effectiveness of Commercial Microbial Products in Enhancing Oil Degradation in Prince William Sound Field Plots Albert D. Venosa, U.S. Environmental Protection Agency.....	353-369
Biodegradation of Volatile Organic Compounds in Aerobic and Anaerobic Biofilters Rakesh Govind, University of Cincinnati.....	370-387
Screening of Commercial Bioproducts for Enhancement of Oil Biodegradation in Closed Microcosms John R. Haines, U.S. Environmental Protection Agency.....	388-403
Alternating Current Electrocoagulation for Superfund Site Remediation Clifton W. Farrell, Electro-Pure Systems, Inc.....	404-415
High Energy Electron Beam Irradiation: An Emerging Technology for the Removal of Hazardous Organic Chemicals From Water and Sludge - An Introduction William J. Copper, Florida International University.....	416-435
Soil Barrier Alternatives Walter E. Grube, Jr., U.S. Environmental Protection Agency.....	436-444
Waste Minimization Assessment Centers - Cost Savings Recommended and Implemented in Twelve Manufacturing Plants F. William Kirsch, University City Science Center.....	445-459
Evaluating Final Covers for Hazardous Waste Landfills Using A Rule-Based Knowledge System James T. Decker, Computer Sciences Corporation.....	460-476
Evaluation of Asbestos Release from Building Demolition Following the October 1989 California Earthquake Bruce A. Hollett, U.S. Environmental Protection Agency.....	477-487
Assessing the Risk of Remedial Alternatives at Superfund Sites - Implications for Technology Demonstrators Patricia Laforvara, U.S. Environmental Protection Agency.....	488-495

SESSION B (Continued)

	<u>Page</u>
Closure of a Dioxin-Contaminated Superfund Site Joyce Perdek, U.S. Environmental Protection Agency.....	496-510
Thermal Desorption Attainable Remediation Levels Paul R. dePercin, U.S. Environmental Protection Agency.....	511-520
Effectiveness of the Stabilization/Solidification Process in Containing Metals from RCRA Electroplating Wastes Ronald J. Turner, U.S. Environmental Protection Agency.....	521-531
Field Assessment of Air Emissions From Hazardous Waste Stabilization Operations Thomas C. Ponder, PEI Associates, Inc.....	532-542
Assessment of the Parameters Affecting the Measurement of Hydraulic Conductivity for Solidified/Stabilized Wastes D.J. Conrad, Alberta Environmental Centre.....	543-559
Ozone-Ultraviolet Light Treatment of Iron Cyanide Complexes Sardar Q. Hassan, University of Cincinnati.....	560-573
Development of LDR Standards for Contaminated Soil and Debris Carolyn K. Offutt, U.S. Environmental Protection Agency.....	574-593
Fate and Treatability of Dyes in Wastewater Glenn M. Shaul, U.S. Environmental Protection Agency.....	594-609
Carbon-Assisted Anaerobic Treatment of Hazardous Leachates A.T. Schroeder, University of Cincinnati.....	610-625
Anaerobic Pretreatment of An Industrial Waste Containing Several VOC's B. Narayanan, John Corollo Engineers.....	626-648
Development of Nonlinear Group Contribution Method for Prediction of Biodegradation Kinetics from Respirometrically-Derived Kinetic Data Henry H. Tabak, U.S. Environmental Protection Agency.....	649-671

SESSION C

	<u>Page</u>
The Effect of Chlorine on NO <sub>x</sub> Emissions From the Incineration of Nitrogen-Containing Wastes William P. Linak, U.S. Environmental Protection Agency.....	672
Pilot-Scale Evaluation of an Incinerability Ranking System for Hazardous Organic Compounds Gregory J. Carroll, U.S. Environmental Protection Agency.....	673
U.S. EPA Incineration Research Facility Update J.W. Lee, Acurex Corporation.....	674
Industry Pollution Prevention Guides Teresa M. Harten, U.S. Environmental Protection Agency.....	675
Inorganic Recycling/Delco Region V Hazardous Waste Recycling Determination Brian A. Westfall, U.S. Environmental Protection Agency.....	676
New Jersey/EPA Waste Minimization Assessments Mary Ann Curran, U.S. Environmental Protection Agency.....	677
Asbestos Control in Buildings Thomas J. Powers, U.S. Environmental Protection Agency.....	678
Supercritical Water Oxidation Deep-Well Reactor Model Development Earnest F. Gloyna, The University of Texas at Austin.....	679
Expansion of RREL Data Base to Include Soil, Debris and Sediment Stephanie A. Hansen, Radian Corporation.....	680
Orismology: The Next Step in Quality Control Guy F. Simes, U.S. Environmental Protection Agency.....	681
Research Opportunities at EPA's E-TEC Facility Daniel Sullivan, U.S. Environmental Protection Agency.....	682
Accessing Leaking Underground Storage Tank Case Studies and Publications Through the EPA's Computerized On-Line Information System (COLIS) Robert W. Hillger, U.S. Environmental Protection Agency.....	683
Metal Value Recovery from Electromachining Sludge Wastes Larry G. Twidwell, Montana College of Mineral Science and Technology.....	684
Bench-Scale Wet Air Oxidation of Dilute Organic Wastes at the Environmental Protection Agency's Test and Evaluation Facility Avi N. Patkar, IT Environmental Programs, Inc.....	685

SESSION C (Continued)

	<u>Page</u>
Characteristics of Bevill Smelting Wastes Henry Huppert, Science Applications International Corp.....	686
Test Program for Evaluation of Foam Scrubbing for Control of Superfund Toxic Gas Releases Pat Brown, Foster Wheeler Enviresponse.....	687
Vapor-Liquid Equilibrium Studies at the U.S. Environmental Protection Agency's Test and Evaluation (T&E) Facility Franklin Alvarez, U.S. Environmental Protection Agency.....	688
Sorption Isotherms for Azo Dyes Onto Activated Sludge Biomass Richard J. Lieberman, U.S. Environmental Protection Agency.....	689
EPA's Synthetic Soil Matrix (SSM) Blending Facility Raymond M. Frederick, U.S. Environmental Protection Agency.....	690
RPM/OSC Summary - Remedial/Removal Incineration Projects Laurel J. Staley, U.S. Environmental Protection Agency.....	691
Treatability Study Results on Soil Contaminated with Heavy Metals, Thiocyanates, Carbon Disulfate, Other Volatile and Semivolatile Organic Compounds Sarah Hokanson, PEI Associates.....	692
Evaluation of Temporal Changes in Soil Barrier Water Content R.J. Luxmoore, Oak Ridge National Laboratory.....	693
Evaluation of Stress Cracking Resistance of Polyethylene Flexible Membrane Liners Yick Halse-Hsuan, Drexel University.....	694
Center Hill Solid and Hazardous Waste Research Facility Gerard Roberto, University of Cincinnati.....	695

SITE DEMONSTRATION OF MICROFILTRATION TECHNOLOGY FOR  
GROUNDWATER CONTAMINATED WITH METALS

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ABSTRACT

The Superfund Innovative Technology Evaluation (SITE) Program has as its major thrust the documentation of reliable performance and cost information for innovative alternative technologies so that they are developed, demonstrated, and made commercially available for the permanent cleanup of Superfund sites. Demonstration projects identify limitations of the technology, applicable wastes and waste media, potential operating problems, and the approximate cost of applying the technology.

A demonstration project was conducted with E.I. DuPont de Nemours & Company, Inc. and the Oberlin Filter Company to evaluate a microfiltration technology for removal of suspended solids from wastewater. The microfiltration system utilized DuPont's Tyvek® T-980 membrane filter media in conjunction with the Oberlin automatic pressure filter. The project was undertaken at the Palmerton Zinc Superfund site in April 1990 to evaluate the ability of the technology to remove zinc from the site's shallow groundwater. Pretreatment of the groundwater to precipitate dissolved zinc and other metals was included as part of the demonstration program. The treated filtrate indicated that the system removed precipitated zinc and other suspended solids at greater than 99.9%, and the filter cake produced during the study passed both the EP Toxicity test and the TCLP.

INTRODUCTION

Over the past few years, it has become increasingly evident that land disposal of hazardous wastes is at least only a temporary solution for much of the material present at Superfund sites. The need for more long-term, permanent treatment solutions as alternatives to land disposal has been stressed by recent legislation such as the Hazardous and Solid Waste Amendments of the Resource Conservation and Recovery Act (RCRA) as well as the Superfund Amendments and Reauthorization Act (SARA) of 1986. SARA directed the U.S. Environmental Protection Agency to establish an "Alternative or Innovative Treatment Technology Research and Demonstration Program," to identify promising technologies, assist with their evaluation, and promote the use of these technologies at Superfund sites. The Superfund Innovative

Technology Evaluation (SITE) Program resulted from that mandate.

The SITE Program is now in its sixth year of demonstrating technologies applicable to Superfund sites with 52 developers conducting 55 projects. The Program offers several advantages to participants, in addition both the Agency and technology developers benefit from the demonstrations. Primary benefits to developers include: experience gained from operating a commercial, field-scale process at a Superfund site; acquisition of valuable regulatory background; increased public awareness of the technology and its capabilities; and documentation of the applicability of the process to cleanup of hazardous waste sites.

Under the Demonstration Program, the developer and EPA participate in a joint venture to operate and evaluate a technology. In general, the developer is required to operate the technology at the selected location while EPA is primarily responsible for writing a demonstration plan, for all sampling and analytical operations, and for reporting and technology transfer activities.

Demonstrations at Federal or State Superfund sites (remedial or removal action sites), EPA test facilities, or at Federally owned sites are encouraged; however, if such sites are not available or not applicable, a developer's facility or a private site may be utilized. EPA is becoming increasingly flexible in the designation of appropriate sites as the Demonstration Program continues to evolve.

#### TECHNOLOGY DESCRIPTION

The demonstration project conducted by DuPont & Company, Inc., in conjunction with the Oberlin Filter Company, features a microfiltration system designed to remove solid particles from liquid wastes, forming a filter cake typically ranging from 30 to 50 percent solids. The filtration unit can be manufactured as an enclosed, trailer-mounted system, requiring little or no attention during operation. The system utilizes Oberlin's automatic pressure filter (APF) combined with DuPont's special Tyvek® T-980 filter media made of spun-bonded olefin. The Tyvek® material is a thin, durable fabric with openings of about one micron. During operation of the unit, it may be possible to get filtration down to the half-micron range or less. A microscopic view of standard Tyvek® material shows it to be only slightly porous, whereas the newer T-980 material has increased porosity and sub-micron filtration capability.

The APF, supplied by Oberlin, provides the support for pumping wastewater through the Tyvek® where solids accumulate to form a filter cake. Contaminated water is pumped across the filter fabric during the filtration cycle until build-up of a filter cake causes the feed pressure to rise to approximately 55 psig. At this point, the APF cuts the feed stream and switches to the cake dewatering cycle where air is blown through the filter cake to dry it prior to discharge. During the discharge cycle, the upper portion of the filter is raised and the filter cake is conveyed out of the filtration chamber on the used Tyvek® filter media as new material is drawn from the clean media roll into the filter chamber. The upper half of the filter then lowers, sealing the chamber above the Tyvek® for the next filtration cycle. The unit cycles through the complete operation automatically so that there is minimal worker exposure to hazardous materials.

The Oberlin APF is available in a variety of sizes from 2.4 square feet up to 36 square feet of filtering area. Similarly, Tyvek® filter media is produced in bulk rolls in several standard widths. The demonstration unit evaluated by the SITE Demonstration Program during the first three weeks of April 1990 was a 2.4-square foot, skid-mounted filter. Treatability tests conducted during July and October 1989, using groundwater from the demonstration site and a synthetic wastewater designed to simulate the groundwater, showed excellent performance by the filter in removing precipitated zinc and other suspended solids. In the July 1989 treatability test, on two separate groundwater runs with mean influent concentrations of 12,433 mg/l and 6,640 mg/l of TSS, the respective effluent concentrations of TSS were 44 mg/l and 23 mg/l.

#### DEMONSTRATION SITE

The microfiltration project was located at the Palmerton Zinc Superfund site in the Lehigh Valley of Pennsylvania. Contamination at the site resulted from smelting operations begun in 1889 by the New Jersey Zinc Company. In 1980 primary zinc smelting operations at the site were terminated, but secondary metal refining and processing operations continued under the ownership of the Zinc Corporation of America, a Division of Horsehead Industries, Inc.

The solid process waste or slag from the smelting operations has been disposed at the site since 1913, and by 1986 approximately 33 million tons of slag had accumulated in a pile nearly 2.5 miles long. Because of elevated levels of heavy metals in the surface water and groundwater of the Palmerton area, the slag pile site was included on EPA's National Priorities List of hazardous waste sites. Samples of the shallow groundwater at the site indicate that zinc is present at the highest levels (300-500 mg/l), while copper (0.02 mg/l), cadmium (1 mg/l), and selenium (0.05 mg/l) are present down to trace levels.

#### TECHNOLOGY EVALUATION

The demonstration was proposed to evaluate the overall ability of the DuPont/Oberlin treatment process to remove zinc from the groundwater at the Palmerton site. In order to accomplish this objective, field studies were designed to produce data relating to four primary aspects of the technology application:

1. Precipitation of metals from the groundwater with emphasis on zinc.
2. Filtration and dewatering of the metals precipitate.
3. Production of filtrate and filter cake to meet applicable disposal requirements.
4. Documentation of operating costs.

During Phase I of the demonstration program, operation of the APF remained unchanged while lime doses for metals precipitation, and ProFix (a filter aid material supplied by EnviroGuard, Inc.) doses for cake buildup and

stabilization were varied. Nine separate runs (treatment batches) yielded data to indicate that optimum chemical addition rates were: lime addition to pH 9; ProFix addition at the rate of 12 grams per liter.

Optimum operating conditions for the APF were set during Phase II of the project. During the rest of the evaluation the chemical addition parameters were held constant. The two items varied during this phase were the pressure at which air was blown through the filter cake to dry it, and the length of time allowed for this function after all water was forced from the filter chamber and air broke through the filter cake. Taking into account the filtrate quality, the solids content of the cake, and the length of time (relating to the cost of treatment) for the drying cycle, the optimum operating conditions were set at a drying (blowdown) time of 0.5 minutes with 38 psig air.

Phase III provided two additional runs at the optimum operating conditions so that reproducibility of the treatment process could be evaluated. The influent zinc concentration in Phase II was reduced from 444 mg/l to 0.22 mg/l (99.95% removal), while in the two Phase III runs the zinc concentration was reduced from 465 mg/l to 0.24 and 0.28 mg/l (99.94 and 99.95% removal). Total suspended solids of 12,500 mg/l in the Phase II influent were reduced to 10.9 mg/l (99.91% removal), and TSS concentrations of 14,300 and 14,000 mg/l in the Phase III tests were lowered to 7.7 and 6.8 mg/l (indicating 99.95% removal).

Phase IV was designed to test the reusability of Tyvek® in the filter system. For this portion of the evaluation program, the filter media was rolled back into the APF following cake discharge. The same area of Tyvek was used for six filtration cycles with no apparent degradation or loss of filtering capacity.

Economic evaluation of the system will be reported in the Applications Analysis Report for this demonstration to be published in the Spring of 1991.

## CONCLUSIONS

During optimum operating conditions the system removed zinc and TSS at a rate of 99.95%. Filter cake solids varied from approximately 30 to 47% with cake solids being 41% at optimum conditions for filtrate quality, chemical addition, and filter cycle time. The filtrate did meet applicable National Pollutant Discharge Elimination System (NPDES) permit limits for discharge to a local waterway for metals and TSS, (maximum daily discharge limits to Aquashicola Creek for zinc and TSS are 2.4 and 30 mg/l) but pH limits were consistently exceeded. The alkaline nature of the ProFix added to the feed stream to increase filtration capability consistently raised the effluent pH to 11.5, thereby violating the 6-9 limit. This condition is not critical, however, and can be mitigated by adding a pH adjustment step as a posttreatment option. The filter cake resulting from the process passed the paint filter liquids test for free liquids at all operating conditions, and a composite cake sample for the total demonstration successfully passed both the EP Toxicity and TCLP tests. A large scale system operating over a longer time might send the filter cake to a metals reclamation facility or a land disposal site.

SITE DEMONSTRATION  
OF THE  
CF SYSTEMS  
ORGANIC EXTRACTION PROCESS

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ABSTRACT

The CF Systems Organic Extraction Process was used to remove PCBs from contaminated sediment dredged from the New Bedford Harbor. This work was done as part of a field demonstration under EPA's Superfund Innovative Technology Evaluation (SITE) program. The purpose of the SITE program is to provide an independent and objective evaluation of innovative waste remediation processes. The purpose of this paper is to present the results of the SITE demonstration of this technology. Results of the demonstration tests show that the system, which uses liquefied propane, successfully removed PCBs from contaminated sediments in New Bedford Harbor. Removal efficiencies for all test runs exceeded 70%. Some operational problems occurred during the demonstration which may have affected the efficiency with which PCBs were removed from the dredged sediment. Large amounts of residues were generated from this demonstration project. Costs for using this process are estimated to be between \$150/Ton and \$450/Ton.

## INTRODUCTION

In 1986, the Superfund Amendments and Reauthorization Act (SARA) was passed to renew the Superfund program. During the reauthorization process, Congress recognized and acted to correct Superfund's heavy reliance on land disposal by mandating the use of innovative or alternative technologies. Section 121 of SARA, Cleanup Standards, requires EPA to favor remedial actions that employ treatment technologies to permanently reduce the volume, toxicity, or mobility of the hazardous substances present at the site. Further, Section 121 encourages EPA to select remedial actions that utilize alternative treatment technologies to the maximum extent possible. The Superfund Innovative Technology Evaluation (SITE) program was established by EPA to identify alternative treatment technologies that can comply with the cleanup standards set forth in Section 121 of SARA.

The SITE program has two main objectives. These are as follows.

1. To conduct demonstrations of promising technologies in order to establish a catalog of reliable performance and cost information.
2. To disseminate this information to those involved with Superfund site remediation.

Solvent extraction has been considered for use in decontaminating hazardous wastes. The idea behind using solvent extraction and other separation technologies is to reduce the amount of material that needs to be disposed of as hazardous waste. This is done by separating waste contaminants from their initial substrate and then concentrating them in a smaller volume. For example, a sediment contaminated with a few hundred parts per million PCBs can be treated as follows using separation. The PCBs can be separated from the sediment using solvent extraction. However, since separation processes do not destroy the PCBs, they must be captured after separation or they will be released into the environment. In capturing the released PCBs, however, they are concentrated on a substrate of smaller volume. As a result, a smaller volume of waste needs to be treated and disposed of. This makes the overall cleanup process more efficient. For example, using solvent extraction to decontaminate soil or sediment containing only a few hundred parts per million PCBs is more efficient than burning many tons of contaminated soil or sediment, especially if the decontaminated soil or sediment can be redispersed on site.

This paper discusses the use of solvent extraction to decontaminate PCB contaminated sediment from the New Bedford Harbor. This work was done under the Superfund Innovative Technology Evaluation (SITE) Program. After describing the CF Systems process and the contamination in New Bedford Harbor, this paper will describe the tests conducted under the SITE demonstration, the results obtained, and the anticipated costs of operation.

## PROCESS DESCRIPTION

The CF Systems Organic Extraction Process is a trailer-mounted, pilot-scale unit designed to treat 20 barrels of contaminated sediments per day. A schematic diagram of the process is presented in Figure 1. CF Systems refers to this test unit as the PCU-20. Slurried sediments from the feed kettle (FK) are pumped through a 1/8" mesh screen to remove oversized particles prior to entering the first stage extractor (E1). The E1 agitator (not shown) mixes the sediments with liquefied hydrocarbon gasses (70% propane/ 30% n-butane, by weight) from the second decanter (D2). Mixing increases the liquid-solid contact surface area and enhances the solvent's ability to extract organics from the sediment. The solvent-organics-sediment mixture flows (by pressure difference) from E1 to the first decanter (D1), where the mixture forms two immiscible layers; solvent-organics on top and sediments at the bottom. The solvent-organics overflow from D1 passes through a fine-mesh paper filter (F1) in order to remove entrained particulates and enters the solvent recovery column (SRC). The sediment flows from D1 to the second stage extractor (E2) and is mixed with freshly recycled solvent to further extract organic pollutants. The solvent-organics-sediment mixture passes from E2 to D2 and separates as per D1. The treated sediments flow from D2 to the raffinate product tank (RPT). The RPT holds treated sediment for subsequent discharge from the PCU-20 system. The solvent-organics mixture passes from D2 to E1.

The pressure in the SRC is low relative to the extraction subsystem. When the solvent-organics stream enters the SRC, the solvent flashes into a vapor state and rises to the top of the SRC. The organics, still in a liquid state, collect at the bottom of the SRC in the column reboiler (CR) along with a small amount of unflashed solvent. As the CR fills, the organics flow to the extract product tank (EPT). The EPT holds the organics for subsequent discharge from the PCU-20 system. The vaporized solvent leaves the SRC and combines with the residual solvent vapors, scavenged from the RPT and EPT and compressed by the secondary compressor (C2). The combined solvent vapor stream feeds the main compressor (C1) and is compressed to a liquid state. The hot, liquefied solvent leaves C1 and passes through a shell and tube heat exchanger located at the column reboiler. The heat exchanger transfers heat of compression from the recycled solvent to the liquid organics to boil off any remaining unflashed solvent. The recycled solvent condenses, leaves the CR heat exchanger and returns to the extraction subsystem via E2.

## SITE DESCRIPTION AND TEST ACTIVITY

New Bedford Harbor has been contaminated for a number of years as a result of industrial activity that has taken place near the harbor in New Bedford, Mass. In 1982, the Harbor was listed on the National Priority List (NPL) due to PCB and toxic metal contamination. PCB contamination ranges from less than 50 ppm

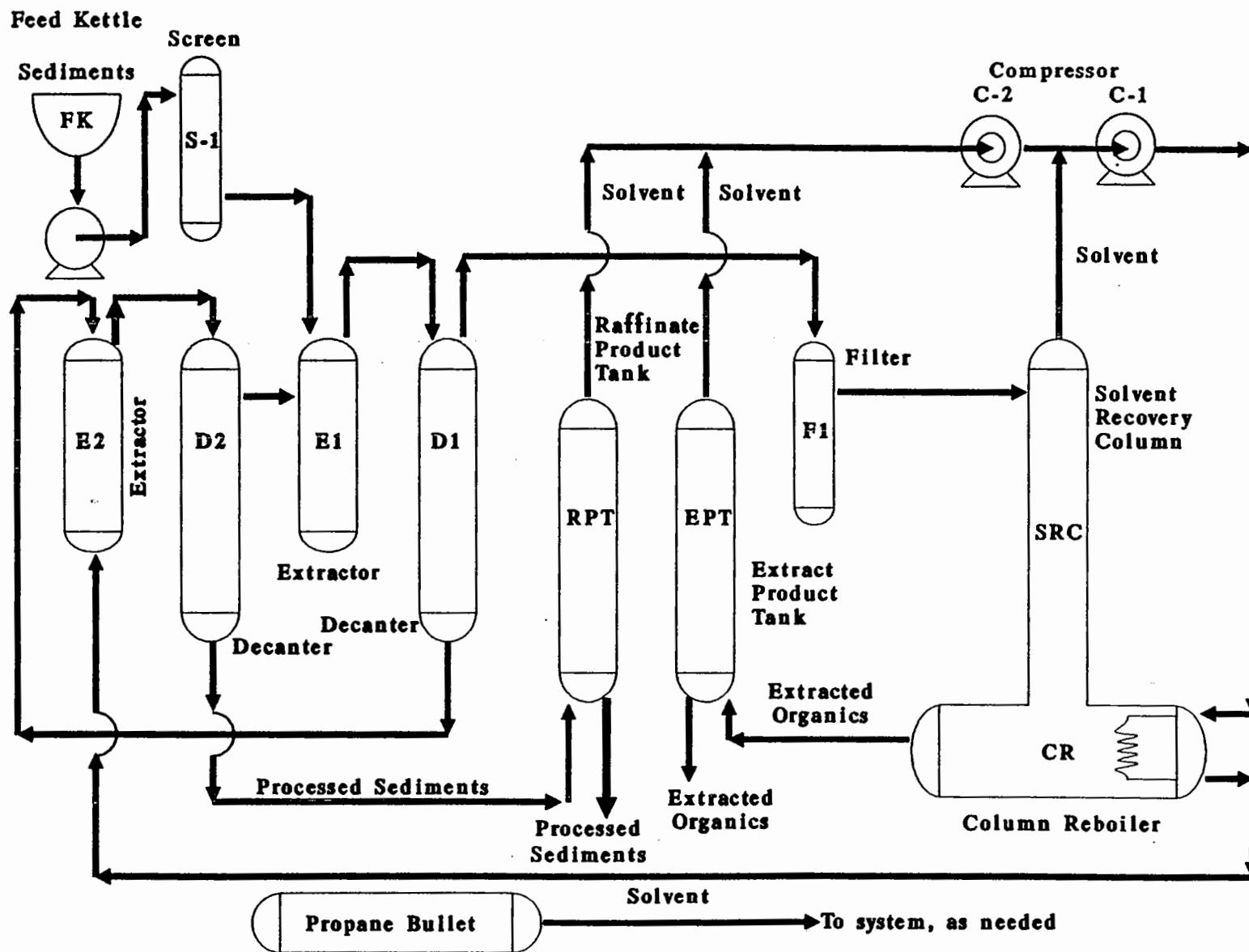


Figure 1. CF Systems PCU-20 simplified process flow diagram

to more than 30,000 ppm, with the majority of the site containing less than 50 ppm PCBs.(1) Roughly 20% of the volume of the contaminated sediment onsite, however, contains between 50 and 500 ppm PCB contamination. Other organic chemicals are present as well. Among these are naphthalene, acenaphthylene, dibenzofuran, fluoranthene, and other polynuclear aromatic hydrocarbons. Metal contamination is also present onsite, although not in high concentrations. Among the metals present at greater than 1 ppm in the sediment are aluminum, calcium, chromium, iron, manganese, potassium, sodium and zinc.(1) The untreated sediment passes the EP Toxicity Test.

In an effort to look at new and better remediation alternatives, the Army Corps of Engineers, who have been cleaning up the site for EPA Region I, decided to conduct a pilot study of the CF Systems process. In a joint effort with the EPA, the pilot study was conducted as a SITE demonstration.

Sediments was dredged from five New Bedford Harbor locations and stored in 55-gallon drums. The raw sediments ranged in total PCB (Aroclors 1242 and 1254) concentration from approximately 160 to 26,000 milligrams per kilogram (mg/kg) on a dry weight basis. In addition, the sediment contained between 30% and 40% solids, was made up of 37% sand, 41% silt, and 22% clay, and had a neutral pH.(1)

Raw sediment was screened to remove particles greater than 1/8" which could damage system valves. Harbor water was then added to produce a pumpable slurry which could be processed by the PCU-20. The prepared sediment was blended to provide three drums of low PCB concentration feedstock (nominally 300 mg/kg) and one drum of high PCB concentration feedstock (nominally 5000 mg/kg). These four drums of sediment were set aside for processing using the CF Systems Pit Cleanup Unit (PCU) during the demonstration.

Using this material, a series of three tests was conducted using 2 different feed concentrations (of PCBs) and three different residence times, where residence time is defined as the number of passes through the PCU. Table 1 summarizes the conditions for each run.

TABLE 1 Demonstration Test Conditions

<u>Test No.</u>	<u>Feed Conc.</u>	<u>No. Passes</u>	<u>Purpose</u>
1	360 ppm	3	Equipment Shakedown
2	350 ppm	10	Produce solid residue containing < 10 ppm PCBs.
3	288 ppm	3	Reproduce the first three passes of Test 2
4	2575 ppm	6	Produce effluent containing 50-500 ppm PCBs
5	Toluene*	3	Decontamination: Produce effluent containing < 10 ppm PCBs.

\* pure toluene was used to decontaminate the PCU-20

The feed and effluent streams were sampled after each pass. A feed-to-solvent ratio of 1.5 was maintained throughout the test. These test conditions were chosen on the basis of earlier bench scale tests conducted by CF Systems which estimated that the PCU-20 could produce a residue containing 17 ppm PCBs from a feedstream originally contaminated with 210 ppm PCBs using 10 passes and the above mentioned feed-to-solvent ratio.

### RESULTS

Extraction efficiencies were at least 72% for all 3 of the test runs. In Test 4, the feedstream containing 2575 ppm PCBs was reduced by 61% to 1000 ppm in 3 passes. Additional passes appeared to continue to reduce the PCB content. After six passes the total reduction in PCB concentration was 92%. Table 2 summarizes the results of the 3 test runs.

TABLE 2 Demonstration Test Results (1)

<u>Test No.</u>	<u>No. of Passes</u>	<u>PCB Feed Conc.</u>	<u>%Reduction</u>
1	N/A	360	Shakedown
2	10	350	89%
3	3	288	72%
4	6	2575	92%
5	3	---	Decontamination

Table 3 shows the pass by pass reduction efficiency achieved.

TABLE 3 Pass by Pass PCB Reduction Efficiency (1)

<u>Test No.</u>	<u>Pass No.</u>	<u>PCB Conc.</u>	<u>%Reduction by Pass</u>
2	Feed	351 ppm	N/A
2	1	77 ppm	78%
2	2	52 ppm	32%
2	3	20 ppm	62%
2	4	66 ppm	N/A
2	5	59 ppm	11%
2	6	41 ppm	31%
2	7	36 ppm	12%
2	8	29 ppm	19%
2	9	8 ppm	72%
2	10	40 ppm	N/A
3	Feed	288 ppm	N/A
3	1	47 ppm	N/A
3	2	72 ppm	N/A
3	3	82 ppm	N/A
4	Feed	2575ppm	N/A
4	1	1000ppm	61%
4	2	990 ppm	1%
4	3	670 ppm	32%
4	4	325 ppm	52%
4	5	240 ppm	26%
4	6	200 ppm	17%

Figure 2 plots extraction efficiency as a function of feed concentration.

Two observations can be made from the above data. First, it is difficult to consistently achieve low effluent concentrations if the PCU-20 has not been thoroughly decontaminated prior to the start of testing. For example, if the test unit is decontaminated by flushing with toluene until the effluent concentration is below 50 ppm, it may be difficult to show much extraction if the feed concentration is at or below 50 ppm. This is because previously extracted organic material is trapped within the system and can result in cross contamination from test to test.

During the demonstration it was noted that the internal system plumbing was coated with oily residue. Since PCBs and other organic contaminants are readily soluble in oily material, this could explain the cross contamination that was observed. This cross contamination may have made it impossible to show a pass-to-pass reduction for most of test 3 and some of tests 2 and 4.

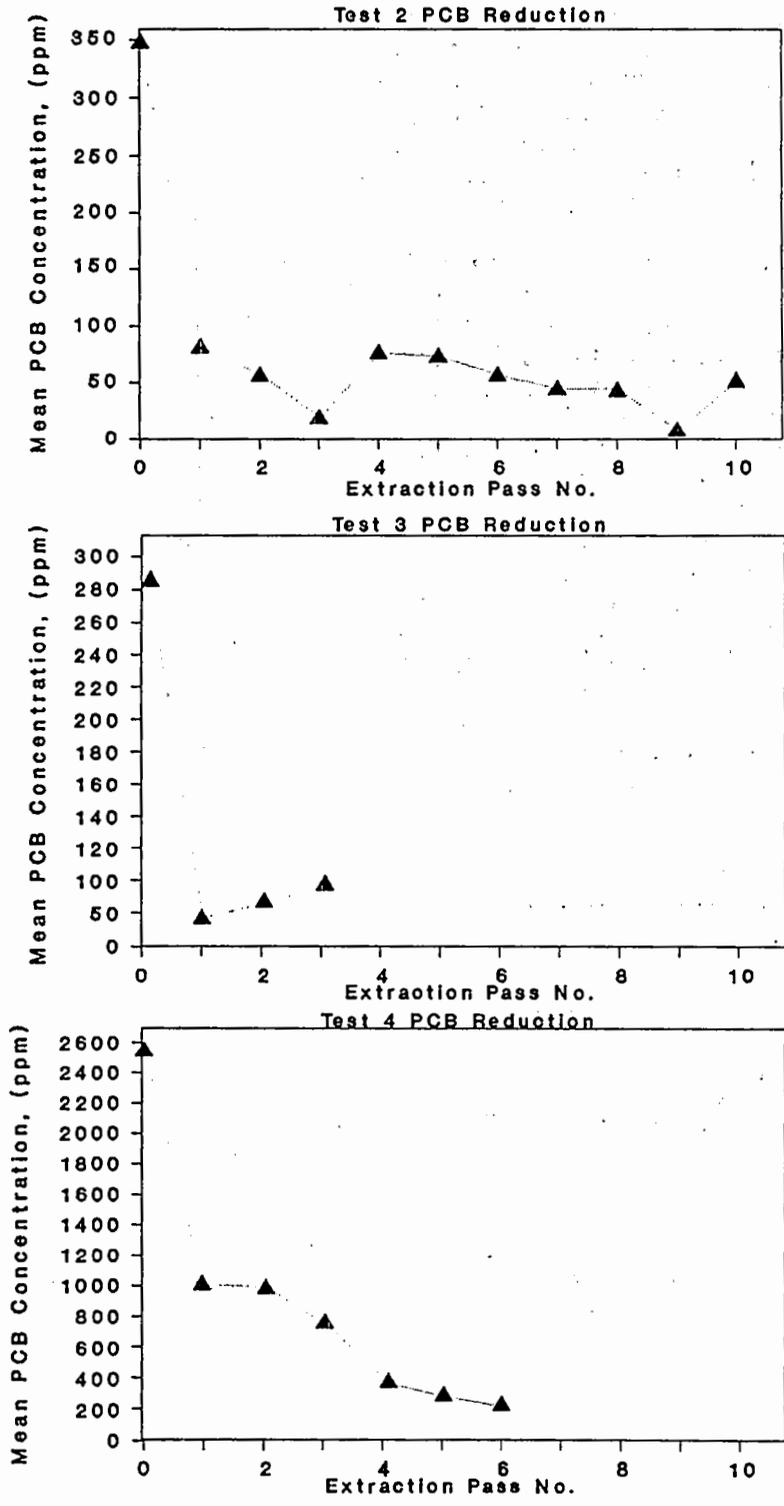


Figure 2. Pass-by-pass extraction efficiency

It is reasonable to assume that some PCBs washed from the extract adhered to tank and pipe walls. PCBs are soluble in oils, and the amount of oil that can adhere to internal hardware could be significant. For example, assume (1) a wetted hardware surface area of 10 square meters, (2) a coating thickness of 1 millimeter, and (3) an oil density of 0.8 grams per cubic centimeter. This is equivalent to 8000 grams of oil accumulation. In this limited throughput demonstration, there were approximately 20,000 grams of oil contained in all four feed drums combined. The demonstration should have included another test using many drums of oil-rich sediments to determine how much extracted oil is required to establish an equilibrated flow through the extract path.

Second, pass-to-pass reduction in PCB contamination is very difficult to measure for two reasons. One, material does not pass through the system uniformly. This is shown most dramatically in Test 4. At the end of pass 2, the concentration of PCBs had only dropped by 10 ppm, from 1000 ppm to 990 ppm. Either the material was not extracted by the system or excess PCBs, which had been retained in the system from earlier test runs, were emitted during this pass resulting in an apparently low extraction efficiency for this test. Material balance calculations suggest that the system irregularly retained and discharged treated sediments. For some passes, as much as 50% of the feed may have been retained in the system, adhering to internal piping and tank surfaces. The sporadic nature of solids accumulation and discharge was not anticipated. If the PCU-20 had modular "add on" extraction stages and was operated in a pass-through mode, solids retention and cross-contamination would be lesser concerns. However, the PCU-20 has only two extraction stages, and recycling is the only way to mimic the effect of a larger number of stages. In future tests, the unit should be partially dismantled at the demonstration's conclusion and inspected in order to reconcile the total solids balance. Larger versions of the PCU-20 have been built and operated by CF Systems. These units do not require that the feed be recycled.

Two, variations in the PCB concentration in the feed contributed to variations in the extraction efficiency. The normal variation in harbor sediment PCB concentration, combined with the variability inherent in the analytical methods used may result in wide variations in the reported extraction efficiency.

Despite these pass-to-pass variations, however, the overall PCB reductions were, as mentioned earlier, high for each test run.

The metals present in the original feedstream remained in the solid residuals after processing.(1) This was expected since this process does not remove metallic contamination. As with the feedstream, this material passed the EP Toxicity Test.

Two other problems occurred during the demonstration. First, dissolved propane caused foaming in the treated sediment product tanks. This caused minor operational problems and can be alleviated with further operational changes.

Second, the volume of waste generated by this process exceeded the volume of material originally treated. While only four drums of waste were treated during the demonstration, 57 drums of process residue were produced. The contents of the residues is summarized in Table 4.

TABLE 4 Residues Produced from the Demonstration (1)

<u>Number of Drums</u>	<u>Drum Contents</u>
6	Toluene (unit decontamination residue)
6	Toluene rinsewater
2	Naphtha-based fuel product and unit residue
15	Sediments
8	Sediments and rinsewater
20	Decontamination water
<hr/> 57	TOTAL

Thirty drums of used Tyvek suits and decontamination debris were also generated as a result of the onsite activities of EPA's evaluation contractor. Although this quantity of waste is unlikely to be generated during normal field operations, it is important to minimize waste generation when using this process. Thirty-two of the 57 drums of residue contained materials related to process decontamination. Refined decontamination procedures that minimize the use of toluene during this step in the process may reduce the volume of toluene and toluene contaminated wastewater produced from this procedure.

Finally, 15 drums of sediment were produced. Under routine operation, this sediment would be redispersed onsite and would not need further treatment.

Costs for this process, as estimated by CF Systems, ranged from \$150/ton to \$450/ton depending upon whether a high volume, low contamination (base case) waste was being treated (\$150/ton) or a low volume high contamination (hot spot) waste was being treated (\$450/ton). (2) Cost analyses for these two cases were prepared by CF Systems and are reproduced below in Tables 5 and 6. The unit costs for treatment presented above do not include the cost of disposing of the concentrated matrix into which the PCBs were extracted. Presumably, this material will be relatively low volume and so will not add greatly to the cost of remediating the site using this technology.

This cost analysis is presented to indicate which factors most affect cost and is not intended to determine a cost for the use of this process at all sites. As determined by CF Systems economic model, the costs associated with operating this process were affected by several factors. These are as follows.

1. The on-stream factor. Fluctuations in this variable significantly affected costs. A decrease in on-stream factor from 85% to 70% increased costs by 20 %.
2. Waste Pretreatment. Elimination of the waste pretreatment step to decrease the solids content can result in a 30% cost savings. Therefore, if the waste is already a pumpable slurry to which no additional water need be added, using this process will be less expensive. This savings occurs as a result of reduced volumetric throughput, reduced equipment sizes and elimination of some pre-and post-treatment steps. Eliminating the need to dilute the waste feed reduces cost more than any other variable in the economic model.
3. Extraction Unit Costs. Costs specific to the extraction unit account for 53% to 68% of total remediation costs using this process.
4. Sediment Excavation and Pre and Post-Treatment Costs. These costs account for 28% to 41% of the total remediation costs.

#### CONCLUSIONS

Several conclusions can be drawn about the PCU-20 as a result of this demonstration. These are as follows.

1. The PCU-20 was capable of removing at least 70% of the PCB contamination in the New Bedford Harbor sediments treated during the demonstration.
2. System decontamination indicates that significant amounts of PCBs may have coated the interior of the process. The resulting cross contamination of the (recycled) sediments may have changed the effluent concentration.
3. The amount of water that must be added to the feed to produce a pumpable slurry affects the cost of the process and the amount of residues generated.

The Demonstration Report and the Applications Analysis Report for the demonstration of this process will be available in June from the USEPA's Center For Environmental Research Information in Cincinnati, Ohio. For further information on this process, please contact:

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TABLE 5 Base Case and Hot Spot Case Summary

<u>Capacity</u>	<u>Base Case</u>	<u>Hot Spot</u>
Raw sludge (40% solids): cubic yards	695,000	50,000
tons	880,000	63,000
Processing Time: years	8.5	1.19
Operating Days	2,591	369
Raw Sludge Feed Rate (@ 40% solids) tons/ operating day	339.5	171.5
Extractor Feed: % Solids	26.7	26.7
total tons processed	1,319,414	94,922
nominal system size (tons/day)	500	250
feed rate (tons/operating day)	509.2	257
Inlet PCB Concentration: ppm	580	10,000
Outlet PCB Concentration: ppm	50	10
PCB Reduction: %	91	99.9
Configuration *	1	2
Processing Fee (1989 \$)		
Facilities	\$5,170,676	\$ 762,496
Extraction	\$62,109,781	\$15,857,695
Pre/Post Treatment	\$46,172,028	\$7,993,608
Contingency	\$11,345,248	\$2,461,380
Project Management	\$5,672,624	\$1,230,690
TOTAL	\$130,470,358	\$28,305,869
Total Life Cycle Unit Cost (\$/ton):		
Extraction Only	\$ 71	\$251
Total	\$148	\$447

NOTES

\*Configuration: 1- Two extraction sections connected in parallel feeding one solvent recovery section connected in series.

2- An extraction and solvent recovery section in series connected in parallel with a second identical extraction and solvent recovery section.

Base Case = High volume of waste /Low contamination level  
 Hot Spot = Low volume of waste/ High contamination level

TABLE 6 Estimated Cost (2)

Case Description (1)	1A Base Case	1B Base Case Reduced On-Stream Factor	1C Base Case No Solids Content Reduction	1D Base Case Increased PCB Removal Efficiency	2 Hot Spot
Waste Volume (Tons)	880,000	880,000	880,000	880,000	63,000
PCB Reduction (%)	91	91	91	98	99.9
Solids Content (%)	27	27	27	27	27
On-Stream Factor (%)	85	70	85	85	85
Remediation Time (weeks)	434	527	280	347	64
Estimated Cost, \$/Ton					
Site Preparation					
Extraction Unit	3.02	2.96	3.02	5.86	47.53
Pre/Post Treatment	1.95	1.95	1.95	1.58	23.57
Excavation	21.44	26.03	13.97	17.14	43.94
Equipment					
Extraction Unit	48.39	58.52	31.53	77.81	173.57
Pre/Post Treatment	23.86	28.98	15.50	19.08	48.91
Startup and Fixed Costs	6.76	8.21	4.39	5.40	13.73
Labor					
Extraction Unit	10.72	13.02	6.97	10.86	33.68
Pre/Post Treatment	10.80	13.11	7.01	9.01	24.09
Supplies & Consumables					
Extract. Unit Utilities	17.06	19.51	11.08	23.91	29.20
Pre/Post Trtmt. Utilit.	2.29	2.78	1.48	1.83	4.68
Analytical	1.98	2.41	1.29	1.59	4.07
TOTALS, \$/Ton	148.27	177.48	98.19	174.09	446.97

- Notes:
- 1) These estimates are only intended for use in planning, scoping, and the inviting of firm bids. The American Association of Cost Engineers has established an accuracy goal of +50% to -30% for preliminary estimates such as these.
  - 3) The costs shown are based on a proprietary model developed by CF Systems, Inc. Cost model outputs are presented in Appendix B for the Base Case and the Hotspot Case.

#### REFERENCES

1. Technology Evaluation Report: CF Systems Organic Extraction System, New Bedford, Massachusetts. EPA/540/5-90/002 January 1990 Cincinnati, Ohio
2. Applications Analysis Report: CF Systems Organic Extraction System, New Bedford, Massachusetts. EPA 540/A5-90/002.

Summary Results of the SITE Demonstration for the  
CHEMFIX Solidification/Stabilization Process

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ABSTRACT

A demonstration of the CHEMFIX solidification/stabilization process was conducted under the United States Environmental Protection Agency's (U.S. EPA) Superfund Innovative Technology Evaluation (SITE) program. The demonstration was conducted in March 1989, at the Portable Equipment Salvage Company (PESC) uncontrolled hazardous waste site in Clackamas, Oregon. Wastes containing lead, copper, and polychlorinated biphenyls (PCBs) from four different areas of the site were treated. Results showed substantial reduction of leachable lead and copper between the untreated waste and treated waste utilizing the Toxicity Characteristics Leaching Procedure (TCLP) test. Long term TCLP results were different than initial results. The effectiveness of this process for immobilizing PCBs could not be determined since the raw waste did not leach PCBs at high concentrations, utilizing the TCLP test. Data from other leaching tests for lead and copper would need to be utilized as input into a site specific ground water model to determine whether solidification/stabilization would be an acceptable remedy for the site. Physical testing results indicated durability in exposed conditions. Valuable lessons were learned which have been useful in subsequent demonstrations.

Description of the CHEMFIX Process

The CHEMFIX process is a patented solidification/stabilization (immobilization) process utilized for the treatment of liquids, sludges, soils, and ashes containing heavy metals and organics. Soluble silicate reagents are normally added to the waste of concern. Three classes of reactions may occur<sup>(1)</sup>:

- Soluble silicates react with cations in the waste matrix to form immobile silicates;
- The silicious setting agents react with the remaining soluble silicates to produce a gel structure;
- Hydrolysis, hydration, and neutralization reactions also occur to further stabilize the waste.

The presence of certain organic constituents may necessitate the use of other additives to the process.

Contaminated soils (screened to minus one inch) were excavated with a backhoe and delivered to an even feeder hopper. The soil was transported to an electrically monitored weigh feeder via a conveyor. The waste was then introduced into a series of mixing equipment apparatus (homogenizer followed by a pug mill) where liquid reagent and dry reagent were introduced. Reagent addition was controlled electronically. Additional make-up water was not always necessary, since the soils from the site were wet from the rainy conditions encountered. Treated wastes are normally transported to an on-site disposal area or transported off-site. CHEMFIX initially rated the capacity of the system utilized at this site for the demonstration at 100 tons per hour (tph).

#### Demonstration Objectives

A Data Quality Objectives (DQO) program was utilized to define the objectives of the CHEMFIX process demonstration before site selection. Based upon performance claims and previous treatment data submitted by CHEMFIX, the following demonstration objectives were established:

- \* Evaluate the ability of the CHEMFIX process to meet or be below land disposal banning levels for heavy metals waste (specifically lead) established by the U.S. EPA;
- \* Determine the effectiveness of the CHEMFIX process (based upon percent reduction) to reduce the mobility of heavy metals (specifically lead and copper) and polychlorinated biphenyls (PCBs) after treatment utilizing the TCLP test;
- \* Determine physical properties of waste treated by the CHEMFIX process for reducing leaching potential and long-term durability indication.

#### Site Description

The PESC site was selected as a demonstration site because the wastes present on the site were suitable for evaluating the demonstration objectives described above. The PESC site operated as a transformer and metals salvage facility from the early 1960's to 1985. Operations at the site involved scrapping and recycling power transformers containing PCBs in cooling oils. Salvageable metals from internal wiring and transformer carcasses were processed and recycled. Transformers and other recycled electrical equipment were burned in a furnace to eliminate insulation and other non-economic elements. Waste transformer oil was used to fire furnaces and metal smelters at the site.

Pre-demonstration sampling activities were geared at isolating waste areas that were sufficiently different in soil type or contaminant concentration to operate the process over a range of characteristics. This approach was aimed at defining the limits of the process for the site waste. Four selected areas were identified as having different characteristics and are described in Table 1. The data showed ranges of contaminant concentrations and a large percentage of debris, which are common on uncontrolled hazardous waste sites. One of the areas contained an ash material as opposed to soil. It should be noted that some lead concentration values encountered were extremely high (up to 139,000 mg/kg).

TABLE 1. Description of Waste Areas Evaluated (pre-demonstration sampling) During the CHEMFIx Site Demonstration

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<u>Area</u>	<u>Description</u>
A	Soil - High lead and copper concentrations (10,000 - 139,000 mg/kg) Medium to high PCB concentrations (100 - 1,940 mg/kg)
C	Soil - High lead and copper concentrations (up to 117,000 mg/kg) High PCB concentrations (up to 1,350 mg/kg)
E	Soil - High lead and copper concentrations (up to 110,000 mg/kg) Low PCB concentrations (<100 mg/kg)
F	Ash - High lead and copper concentrations (40,000 - 136,000 mg/kg) Medium PCB concentrations (200 - 300 mg/kg)

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#### Demonstration Program

Ten cubic yards of soil from each of areas A, C, and E and ten cubic yards of ash from area F were individually processed for this demonstration. The material was excavated, screened to minus one inch, and mixed on the ground by a backhoe to better homogenize the waste before treatment. Only a total of forty cubic yards of material were processed to minimize the amount of treated material that would be generated on-site. Process mixing performance was expected to be negatively impacted by processing such limited quantities of waste in a high capacity system, because calibration time would be limited. Area C soils were selected as the waste type where the majority of the physical and chemical testing methods would be performed.

The screened material was visually estimated to be about 30% of the total volume of material excavated. The quantities of all materials utilized were documented for mass balance purposes.

#### Sampling and Analysis Program

Raw soil samples were obtained the day of the demonstration and treated soil samples were taken immediately after processing. Leaching test samples were formed in plastic or cardboard molding tubes to eliminate destruction of samples or perceived interferences of leaching results from coring operations. Table 2 describes the leaching tests utilized in the demonstration.

TABLE 2. Leaching Test Utilized in the CHEMFIX SITE Demonstration

<u>Name of Test</u>	<u>Reference</u>	<u>Description</u>
TCLP	40 CFR Part 268	Ground material subject to 18 hour extraction process with acetic acid leachant to simulate co-disposal environment with municipal waste
MEP	EPA method 1320 (SW 846)	Ground material subject to 24 hour extraction with acetic acid leachant followed by nine sequential extractions with acidic rain simulated leachant
ANS 16.1	American Nuclear Society 16.1	Monolithic material placed in distilled water that is replaced over discrete time intervals (diffusion model)

Baseline physical and chemical tests were performed on the raw waste for comparison to treated waste samples. Table 3 lists the physical and chemical tests utilized in the demonstration. An air monitoring system with polyurethane foam (PUF) was employed to determine if PCBs were volatilized during the mixing or curing process.

TABLE 3. Physical and Chemical Test Utilized in the CHEMFIX SITE Demonstration

<u>Name of Test</u>	<u>Reference</u>	<u>Description</u>
Unconfined Compressive Strength (UCS)	ASTM D1633	Used to assess structural integrity of monolith
Hydraulic Conductivity	EPA draft protocol	Used to assess resistance of material to water flow
Wet/Dry Resistance	ASTM D 4843	Indication of durability in wet/dry environment
Freeze/Thaw Resistance	ASTM D 4842	Indication of durability in freeze/thaw environment
Oxidation/Reduction	EPA method 9045 (modified)	Determine oxidation/reduction state of waste matrix
Electrical Conductivity	ASA 10. - 3.3	Determine amount of ionic materials present in solution

## Demonstration Results

### Leaching Testing

Two values were established as the criterion for determining if the treated waste met the U.S. EPA land ban criteria for lead. The first value was .51 mg/L (TCLP leachate) based on the U.S. EPA standard for listed (F006 sludges) hazardous waste<sup>(2)</sup>. A second, higher level of 5.0 mg/L was arbitrarily chosen to recognize that soils may be more difficult to treat than sludges. 65% of all samples tested from areas A, C, E, and F passed the 0.51 mg/L standard and 70% passed the higher standard of 5.0 mg/L.

Substantial reductions in the leachability of lead and copper in the raw waste, as determined by the TCLP, were observed. Table 4 shows that lead reductions ranged from 94% in area E to 99% in areas A, C, and F. Copper reductions ranged from 95% in area C to 99% in areas A, E, and F. Data from these TCLP results need to be kept in the limited perspective that this test simulates a leaching environment involving co-disposal with municipal waste. This scenario may not have applications for the PESC site.

TABLE 4. Mean Concentrations of Lead and Copper from the CHEMFIX Demonstration

	Untreated Waste (total)	TCLP From Untreated Waste	TCLP From Treated Waste	Percent Reduction of TCLP Extractable Metal
<u>Area A</u>				
Lead	21,000 mg/kg	610 mg/L	<.05 mg/L	99
Copper	18,000 mg/kg	45 mg/L	0.57 mg/L	99
<u>Area C</u>				
Lead	140,000 mg/kg	880 mg/L	2.5 mg/L	99
Copper	18,000 mg/kg	12 mg/L	0.54 mg/L	95
<u>Area E</u>				
Lead	92,000 mg/kg	740 mg/L	47 mg/L	94
Copper	74,000 mg/kg	120 mg/L	0.65 mg/L	99
<u>Area F</u>				
Lead	11,000 mg/kg	390 mg/L	0.10 mg/L	99
Copper	33,000 mg/kg	120 mg/L	0.60 mg/L	99

The reduction in mobility of PCBs, based on the TCLP, could not be determined since the PCBs essentially did not leach in the raw waste. More stringent leaching or extraction tests would be necessary to determine the effectiveness of this process for stabilizing PCBs.

Data from the MEP test were non-conclusive. In many instances, a criterion of 5.0 mg/L for lead was exceeded during the first extraction, but was not exceeded during the nine subsequent leaching extractions.

Data from the ANS 16.1 test for lead and copper are presented in Table 5. Leaching data are calculated into a leachability index (LI) which is the negative logarithm of the effective diffusivity coefficient. The treated material successfully exceeded the Nuclear Regulatory Commission (NRC) criterion for LI of six by several orders of magnitude<sup>(3)</sup>. However, the acceptability of these results, based on protection of the public health and environment, should be judged only after leaching values (fluxes) are incorporated into a site specific ground water model.

TABLE 5. ANS 16.1 Leachability Index (LI) Data from the CHEMFIx SITE Demonstration

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<u>Contaminant</u>	<u>LI</u>
Lead	13.2
Copper	15.2

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#### Chemical Testing

Data from chemical testing between the raw and treated material can be seen in Table 6. Oxidation/reduction potential of the treated waste was less than the raw waste. Conductivity of the treated waste was considerably higher than the raw waste, indicating that ions are leaching from the treated material. However, loss of ions into solution may not be of concern, depending upon the chemical nature of the ions. The pH of the raw waste, 6.6, increased to 11.5 after reagent addition. The pH of the treated material was not impacted to a large degree by the acetic acid leachant of the TCLP.

The air monitoring data suggested that there was no significant volatilization of PCBs during the treatment operations at the site. It should be noted that the wet, cool temperature environment encountered during the demonstration would not promote volatilization.

#### Physical Testing

The results of the physical test performed on the treated wastes are shown in Table 6. Weight loss during wet/dry and freeze/thaw cycle testing was less than one percent. These data indicate durability in an exposed environment. Unconfined compressive strength (UCS) values ranged from 27 pounds per square inch (psi) to 307 psi. The U.S. EPA guidance value for solidified/stabilized waste for UCS is 50 psi<sup>(4)</sup>. Hydraulic conductivity of the treated material was in the range of  $1 \times 10^{-6}$  to  $1 \times 10^{-7}$  cm/sec. Acceptable hydraulic conductivity values should be compared to in-situ permeability measurements, which were not obtained at the site. The volume increase in the waste excavated material after treatment ranged from 20 to 50 percent.

TABLE 6. Physical and Chemical Properties of Treated and Untreated Wastes from Area C of CHEMFIx Demonstration

	Area C	
	Untreated Wastes	Treated Wastes
Eh (millivolts)	290	24
Conductivity (umhos/cm)	130	3200
pH	6.6	11.3-11.5
28-day UCS (psi)	N/A	27-307
Wet/dry stress weight loss	N/A	<1%
Freeze/thaw stress weight loss	N/A	<1%
Permeability (cm/sec)	$10^{-4}$ to $10^{-6}$	$10^{-6}$ to $10^{-7}$
N/A Not Applicable		

Long Term Leaching Testing Results

Treated samples from area C were subjected to the TCLP test and the ANS 16.1 test after six months and one year. Leaching values for the TCLP test progressively increase over time as can be seen in Table 7. The author feels however, that surface carbonation reactions may occur on these samples over time and possibly interfere with the true leaching results. If however, the leaching results are true, regulatory agencies may want to consider utilizing longer cured samples in treatment evaluations. Leachability index results were consistent from the 28 day sample through the one year sample, indicating no change in physical or chemical behavior.

In an effort to reduce uncertainty of the long term leaching of stabilized materials, the SITE program has established long term testing apparatus to expose the stabilized material to extreme weathering conditions over time. Laser holography, X ray diffraction and acoustic vibration are some of the testing procedures that weathered samples will encounter.

TABLE 7. LONG TERM LEACHING RESULTS FOR LEAD FOR AREA C

SAMPLE	TCLP MEAN CONC. (mg/l)	LEACHABILITY INDEX
Raw Soil	880.0	NA
28 day cured	2.5	13.2
6 month cured	14.0	13.7
1 year cured	24.0	13.8

N/A - Not Applicable

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### Lessons Learned

Several potential problem areas for performing large scale demonstrations of stabilization processes were observed during the demonstration planning and implementation. The following is a brief summary of general problem areas:

\* Debris such as metal wire or broken bricks were encountered and needed to be physically separated from the contaminated soil to eliminate leaching test interferences

\* PCBs were not leachable in the raw waste utilizing the TCLP test, making treatment performance efficiencies difficult to calculate

\* The demonstration occurred at a lower processing rate than the equipment was designed for, therefore accurate calibration of the mixing process during the short processing time was not possible

\* Chemical concentration results from preliminary sampling at the site varied from the actual sampling results during the demonstration, negating optimization of the binding mixture utilized

\* Testing methods for determining mixing efficiency are not well developed

### Conclusions

The majority of the treated waste samples from the CHEMFIX solidification/stabilization process met land ban standards criteria established for the demonstration. Reductions of leachable lead, judged by the TCLP test, ranged from 94 to 99%. Data from the ANS 16.1 test successfully exceeded the NRC criterion of six by several orders of magnitude, but these data need to be incorporated into a site specific ground water model before the performance of the process can be judged for this site.

The CHEMFIX process generally produced treated material with acceptable physical properties. The treated material had properties that indicated long-term durability in exposed environments. Volume increase in the excavated material after treatment ranged between 20 to 50%. Valuable lessons were learned during the preparation and implementation of this demonstration that have minimized problems on subsequent demonstrations.

### References

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### Acknowledgements

The author would like to acknowledge the following people in implementing this demonstration: Mark Evans, Nancy Willis, and Shin Ahn of PRC Inc., Danny Jackson and Debra Bisson of Radian Corporation, Guy Simes and Dean Neptune of EPA's Office of Research and Development, and Paul Lo and Phil Baldwin of CHEMFIX Technologies Inc.

SOIL VAPOR EXTRACTION: AIR PERMEABILITY  
TESTING AND ESTIMATION METHODS

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**ABSTRACT**

Soil-air permeability is a critical parameter used to assess the feasibility of soil vapor extraction (SVE) technology for sites where volatile organic compounds are present in the vadose zone. Field, laboratory, and empirical correlation methods for estimating soil-air permeability have been reviewed for their appropriateness in determining SVE feasibility and for the development of SVE system design criteria.

Empirical methods are available to derive estimates of soil air permeabilities from soil grain size distributions, hydraulic conductivity measurements, or pump test drawdown data. Although these techniques provide data which serve to determine if the use of SVE should be excluded from further consideration, they do not provide adequate data for system design criteria development. Laboratory soil-air permeability tests are also inappropriate for SVE system design because of the variability in soil field permeability and the non-representative nature of soil cores collected in the field. Field techniques employed for determining soil-air permeability in surficial soils are likewise inappropriate for the evaluation of contaminant releases that have migrated to depths of greater than one meter. The in situ field borehole permeability techniques used by petroleum engineers, and subsequently modified for use at relatively shallow soil depths, hold the most promise for application to SVE design.

Although most SVE vendors and contractors use some type of soil permeability estimation or measurement technique, description of the use of these techniques in conjunction with SVE system design is often of a proprietary nature. Additionally, no standard technique for uniform measurement or reporting of soil-air permeability is available. Shell Development Co. and Shell Oil Co. (Shell) have developed a practical approach to the design, operation, monitoring of SVE, which has been detailed in a paper by Johnson, Stanley, Kemblowski, Byers, and Colthart (1, 2). The determination of soil-air permeability is a critical component of

this approach, and a procedure is presented for the calculation of soil-air permeability. The Shell method also provides a basis for refining the soil-air permeability measurement techniques used in the remediation industry. However, successful implementation of the methodology as a comparative site evaluation tool for SVE system design could benefit from the development of standardized guidelines for the construction of vapor extraction wells and monitoring wells.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and is approved for presentation and publication.

## INTRODUCTION

Soil vapor extraction (SVE) has become a commonly used technology for the remediation of soils contaminated with volatile contaminants. Critical to the application of SVE technology at a particular site is the ability to achieve adequate vapor flow through the contaminated zone. Soil-air permeability describes how easily air will flow through the soil and is expressed in units of length squared ( $\text{cm}^2$ ). Vapor flow rates through porous media, such as soil, are dependent upon soil characteristics including porosity and permeability, as well as gas properties such as viscosity, density, and pressure gradients. Gas is a fluid and as such its flow rate through porous media is commonly characterized by Darcy's law. Darcy's law is valid for laminar, isothermal flow that is uniformly distributed across a given cross sectional area. The general formulation of Darcy's law for saturated fluid flow in one dimension is (2):

$$q = (kA/\mu)(dP/dm) \quad (1)$$

where:

q = flow rate ( $\text{cm}^3/\text{sec}$ )  
k = permeability ( $\text{cm}^2$ )  
A = cross-sectional area ( $\text{cm}^2$ )  
 $\mu$  = viscosity ( $\text{g}/\text{cm-sec}$ )  
 $dP/dm$  = pressure gradient ( $(\text{g}/\text{cm-sec}^2)/\text{cm}$ )

Since air permeability will control the decision to implement SVE technology at a contaminated site to a large degree, the importance of the air permeability measurement or estimation technique is evident. To date, no standard method has been advanced for determining soil-air permeabilities for sites at which SVE techniques might be applied. In fact, many SVE technology vendors utilize proprietary techniques and methods for estimating cleanup times and establishing system design criteria. The conflicting methods and claims pose problems to regulators required to make judgements on the appropriateness of a proposed SVE system design. To provide some guidance with regard to air permeability test methods, a review of available techniques was undertaken. This paper provides an initial assessment of the

applicability of various air permeability determination methods. Soil-air permeability estimation and testing methods considered include: correlation to empirical soil properties such as soil grain size distribution or soil hydraulic conductivity; laboratory measurements; and in situ field measurements. Table 1 lists some air permeability test methods and summarizes the limitations with regards to site evaluation and SVE feasibility determination.

#### CORRELATION METHODS

Soil air permeability may be estimated from known physical characteristics of the soil sample, such as the grain size distribution or saturated hydraulic conductivity.

Massman (4) discusses the use of a linear correlation between both soil grain size distribution analyses or saturated hydraulic conductivity and soil air permeability. These methods do not account for decreases in the air permeability due to increased moisture contents or visa versa, nor do they account for in situ bulk density, soil structure, or heterogeneity of the subsurface soils. The variability in permeabilities associated with differing soil characteristics can be accounted for by sampling throughout the area where SVE is to be applied and averaging the resulting air permeabilities.

The use of saturated hydraulic conductivity values to estimate air permeability is subject to several additional sources of error including soil moisture content, swelling soils, and gas slippage. First, both air permeability and saturated hydraulic conductivity are influenced by the soil water content. Hydraulic conductivity generally increases while air permeability generally decreases as the water content of a soil increases (5, 6). The second source of error results from the interaction of soil particles with water. Theoretically, the intrinsic permeability for water is only a function of the medium. However, in some cases, water alters the structure of clay, due to expansion as the water content increases. This dramatically reduces the intrinsic permeability. Therefore, the correlation between saturated hydraulic conductivity and air permeability would not be valid for soils with an appreciable content of expandable clay. The third source of error in this method is due to the "slippage" of gas as they pass along the soil pore wall. This factor commonly known as the "Klinkenberg effect", accounts for the soil air permeability having a greater value than the liquid permeability at low gas pressures in fine grain soils. Darcy's law assumes that the flow velocity at the pore wall is zero. However, this assumption becomes invalid, and the "Klinkenberg effect" becomes significant in materials having an intrinsic permeability less than 10 millidarcies (15).

Field data from aquifer slug tests or drawdown tests can be used to estimate the soil air conductivity and soil gas storage coefficients using graphical curve matching techniques analogous to the Theis, Hantush, or

Jacobs methods developed for groundwater pump tests. The Theis curve matching method (7) is commonly used in unsteady well hydraulics. For unsteady flow applications, Darcy's law is expressed as a partial differential equation that includes time as a variable. However since these tests are performed in the saturated zone they do not provide a good indication of unsaturated zone permeability.

Correlation methods provide a quick means of assessing the relative permeability of soil but would not be appropriate for SVE system design criteria development. However, both the grain size and saturated hydraulic conductivity correlation methods only provide an order of magnitude estimate (4).

#### LABORATORY METHODS

Laboratory methods used for the determination of air permeability were pioneered in the petroleum industry (8, 9) and adapted for use in agriculture (10, 11). Although the petroleum industry designed air permeability measurement apparatus for relatively undisturbed porous rock samples, and the agricultural industry designed apparatus for undisturbed soil samples, the general features of the laboratory tests are similar. Samples are placed in a pressure vessel (permeameter) and saturated with water or another wetting fluid and air is injected to force the wetting fluid out of the sample (desaturation) while air flow rates and air pressure in the sample are measured. Measurements of porosity, air flow and pressure differential are used in Darcy's law to estimate the air permeability as a function of water content.

Laboratory air permeability measurement methods are subject to significant error since air permeability is sensitive to the bulk density, and the structure of the soil. These soil characteristics are altered when a subsurface sample is exhumed and placed in the permeameter. In addition, laboratory measurements can not account for heterogeneities encountered at a site that affect the overall soil air permeability of a particular location. Use of laboratory permeability measurements for SVE system design is not considered appropriate because of limitations in the methods to account for spatial variability associated with field conditions.

#### FIELD METHODS

There are a variety of in situ field methods that have been employed for the determination of soil air permeability. All of the methods rely on measuring the difference between the ambient atmospheric pressure and the soil air pressure in the soil during subsurface vapor transport. The methods described in this section include: air injection testing; subsurface

barometric fluctuation measurements; oil field tests, such pressure build-up tests, and drawdown tests; and a soil vacuum extraction method (1).

#### AIR INJECTION

Air injection tests are generally performed on surficial agricultural soils, utilizing equipment consisting of a compressed air tank and a gas flow/pressure regulator attached to a cylinder which is inserted into the soil (12, 13, 14). The pressure differential is measured before and after a known volume of air is injected through the cylinder into the soil over a given time period. The soil air permeability is estimated using Darcy's law with measured and known values for the pressure differential, air flow rate, cross-sectional area of the cylinder, and viscosity of the air. Although air injection testing has been applied principally to surficial soils it can be applied to subsurface investigations.

The advantages of surficial air injection testing are relatively portable measurement equipment, quick measurements, and low cost. However, air injection testing may not be appropriate to determine the soil air permeability needed for SVE implementation or developing SVE system design criteria. When air is injected the soil particles may tend to disperse and yield a higher permeability value. Therefore, the permeability measured by injecting air into soil may not be the same as the permeability measured by vacuum suction of air from soil resulting in lower values.

#### BAROMETRIC FLUCTUATIONS

Monitoring changes in barometric pressure can be used to determine the vertical air permeability by finding an effective "pneumatic diffusivity" at prevailing soil porosity and moisture content (15). The pneumatic diffusivity is analogous to the hydraulic diffusivity terms used in groundwater flow. Barometric pressure changes are measured using specially designed piezometer wells nested within the unsaturated soil. Manifold manometer systems are used to measure air pressure at each of the screened levels. The permeability is estimated using an iterative process that equates the air flux between adjoining subsurface layers where the barometric pressure was measured. Weeks (15) provided a computer program that solves for the vertical air permeability using a trial and error numerical solution.

One major limitation of applying this method is that the manometer system can only measure barometric pressure differences during the normal diurnal barometric pressure change if the unsaturated zone is greater than 20 meters thick and has at least one layer with a permeability less than 2 to 3 darcies. However, permeabilities this low would probably limit the effectiveness of SVE technology. For thinner, more permeable, unsaturated soils, barometric pressure differences can only be obtained during the passage of an atmospheric front in which the pressure changes a few millibars in less than an hour. Since it is not feasible to predict the occurrence of atmospheric conditions, and since this test principally address vertical flow, the use of this technique for SVE is not appropriate.

## OIL FIELD TEST METHODS

The petroleum industry has used a number of in situ field tests to determine air permeability. Most of the tests are performed using one or more potential gas production wells. Production well natural gas differs from SVE gases, in that natural gas in subsurface geological layers is under higher pressures and temperatures than the organic vapors encountered in the vadose zone. Thus, the modeling of natural gas flow and air permeability estimates of natural gas production reservoirs usually incorporates parameters for gas compressibility and temperature, not found in the vapor transport equations used for SVE (1,2). Two commonly used methods of determining air permeability of gas producing formations are the pressure buildup test and the drawdown test.

Pressure build-up and drawdown tests can be performed using a single well or by use of an extraction well and monitoring wells. The physical relationship between the vapor extraction well and the monitoring well used in drawdown tests is illustrated in Figure 1.

### Pressure Buildup Test

The pressure buildup test is conducted by closing a gas well that has been producing gas at a constant rate for a given period of time, and monitoring the down hole pressure increase after the well is closed or shut-in (16). Gas flow in the well is modeled by Darcy's law with radial gas flow. The pressure buildup test is considered to be the result of two superimposed effects: the pressure drawdown caused by the initial gas flow from the well, and the increase in pressure that occurs when the well is closed or shut-in. The pressure increase is modeled as a gas injection with a flow rate equal in magnitude and opposite in sign (or direction) to the gas flow rate from the well during pressure drawdown. There are a number pressure time relationships presented in natural gas engineering texts (17, 18, 19).

The pressure build-up tests most likely are not applicable to soil air permeability testing for SVE technology since confined deposits of vapor are not usually associated with contaminant releases. The vapor pressures found in contaminated soils may not create a significant pressure build-up when the vapor extraction well is shut-in.

### Pressure Drawdown Test

The pressure drawdown test is another common oil field method for determining air permeability (17, 18, 19). In this test, gas is extracted from a well at a constant flow rate while the pressure reduction in the well is observed over time. Again, as in the case of the pressure build-up test, the pressure versus time relationship is modeled using Darcy's law applied to radial gas flow. Additional factors are included in the modeling equation to account for the compressibility of the gas, and porosity variations near the well screen cause by well installation (skin effect). The pressure buildup test is sometimes preferred in oil field work over a

pressure drawdown test, since it is difficult to achieve the constant gas flow rate out of the well required for a drawdown test (16).

The mechanics and modeling of the drawdown test are similar to those used to determine soil air permeability proposed by Johnson et al. (1, 2). The additional gas compressibility and skin effect factors are probably not significant in determining air permeability of low pressure vapors extracted from shallow wells.

## SVE AIR PERMEABILITY MEASUREMENT METHODS

### SHELL'S APPROACH

The soil air permeability test developed by Shell (1, 2) for SVE technology is similar to the oil field drawdown test. In the case of the Shell method, the drawdown or vacuum pressure ( $P'$ ) is measured in a monitoring point at a distance ( $r$ ) from the vapor extraction well, while removing vapors at a constant rate ( $Q$ ). The equation that approximates expected pressure changes over time is:

$$P' = Q/(4\pi m(k/\mu) [-0.5772 - \ln[(r^2 \epsilon \mu)/(4kP_{atm})] + \ln(t)] \quad (2)$$

where:

- $P'$  = gauge pressure ( $g/cm\text{-}sec^2$ )
- $Q$  = flow rate from vapor extraction well ( $cm^3/sec$ )
- $m$  = stratum thickness (screen<sub>2</sub>length) (cm)
- $k$  = soil air permeability ( $cm^2$ )
- $\mu$  = dynamic viscosity of air ( $g/cm\text{-}sec$ )
- $\pi$  = 3.142
- $r$  = distance of sample probe well from vapor extraction well (cm)
- $P_{atm}$  = ambient atmospheric pressure ( $g/cm\text{-}s^2$ )
- $\epsilon^{atm}$  = vapor filled void fraction (0.0 - 1.0)
- $t$  = time (sec)

As in the case of the oil field drawdown method, soil air permeability ( $k$ ) can be estimated graphically from field data. The first method assumes that the volumetric vapor flow rate ( $Q$ ) from the extraction well and the thickness of the screened interval ( $m$ ) from which vapors are being extracted are known. The second method is applied when  $Q$  and  $m$  are unknown. Both methods rely on calculating the slope of the regression line that relates gauge pressure,  $P'$ , measured at a sample probe well to the natural logarithm to the time,  $\ln(t)$ , from the initiation of vapor extraction. The relationship of  $P'$  versus  $\ln(t)$  is based on equation (1), where the slope (A) is:

$$A = Q/4\pi m(k/\mu) \quad (3)$$

and the y intercept (P' axis) of the regression line is:

$$B = Q/4\pi m(k/\mu) [-0.5772 - \ln(r^2 \epsilon \mu / 4kP_{atm})] \quad (4)$$

If the flow rate (Q) and the screened interval (m) are known, the soil air permeability is calculated by solving equation (3) for k.

$$k = Q\mu/4A\pi m \quad (5)$$

If flow rate (Q) and the screened interval (m) are not known then the soil air permeability is calculated by substituting equation (3) into equation (4) and solving for k.

$$k = r^2 \epsilon \mu / 4P_{atm} [\exp(B/A + 0.5772)] \quad (6)$$

All of the parameters used to estimate permeability are measured in the field with the exception of the dynamic viscosity of air which is estimated as a function of air temperature.

Permeability values should be measured at a number of locations around the vapor extraction well and then averaged to provide a reasonable estimate of the areal variability soil air permeability.

#### TESTING METHOD APPLICATION CONSIDERATIONS

Air permeability testing as suggested by Shell (1, 2), assumes that as the time from initiation of soil vapor extraction increases, the vacuum pressure in the subsurface increases (ie: the absolute pressure becomes more negative). However, this relationship may not always hold during the time intervals over which SVE vacuum pressure data may be measured in the field (days, weeks and months of continuous operation). As the time over which SVE is implemented increases, soil moisture is removed from the subsurface, increasing the effective porosity. As the effective porosity increases, the subsurface vacuum pressure may decrease (become more positive). Therefore, it is important to specify that the test be conducted for a short period.

The time interval over which air permeability measurements are made should be long enough to extract at least one pore volume of air, yet short enough not to be hampered by: variations in atmospheric pressure, and effective porosity changes that occur after rainfall and when soil air moisture condenses and evaporates during diurnal temperature changes.

Because it is often difficult to maintain a constant vapor extraction rate during SVE operation, variations in the vapor extraction rate should be recorded and used when evaluating data. The sensitivity of the air

permeability measurement will be reduced as the variations in the vapor extraction rate increase.

SVE is often operated concurrently with groundwater extraction and treatment. If the groundwater extraction causes an increasing cone of depression in the area where SVE is being implemented, then, over time, the soil volume susceptible to vacuum pressures may increase, and the perceived soil air permeability may vary.

The Shell soil-air permeability method provides a valuable tool for SVE site assessment and design criteria development. More wide spread application of these test methods might result if additional guidance or standardization were provided for if standardized:

- o extraction well diameter
- o screened length
- o monitoring point diameter
- o radial spacing of monitoring points around extraction well
- o extraction rates
- o measurement intervals and period

In addition, to allow for correlation of data to other sites, critical soil measurements should be obtained during extraction well installation including soil density (standard penetration test), soil grain size distribution (sand, silt and clay), and soil moisture content.

#### CONCLUSIONS

Soil air permeability data are critical to the assessment of SVE feasibility and subsequent development of SVE design criteria at a particular site. Use of correlation techniques to estimate air permeability are appropriate for use in first step estimation of appropriateness of SVE. Conversely, laboratory soil-air permeability determination and air injection field tests are generally not appropriate for determining the feasibility of SVE technology. The best estimates of soil-air permeability would probably be obtained from in situ field drawdown tests modified for use in the vadose zone.

For sites where SVE is feasible, a field soil-air permeability test such as that described by Johnson et al. (1990) should be undertaken to develop SVE design criteria. The field program should identify the data collection requirements and at a minimum the following guidelines should be followed.

- o Field measurements of vacuum pressure from at least three monitoring wells spaced around a vapor extraction well should be used.
- o A constant extraction well flow rate should be maintained for the duration of the test.
- o Several air permeability measurements should be made over the site to ensure that the lateral heterogeneity of the site is assessed.

- o Several air permeability measurements should be made over the site to ensure that the lateral heterogeneity of the site is assessed.

The basic air permeability tests provide an order of magnitude estimate for application of SVE. Depending on site conditions and contaminant distribution the use of vapor flow modeling techniques may be required to obtain an adequate understanding of the vapor flow regime necessary to achieve remediation. Likewise, the use of laboratory treatability studies may be required in order to develop accurate estimates of cleanup times.

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TABLE 1

AIR PERMEABILITY TEST METHODS

Method Reference	Field or Lab Parameters	Assumed Parameters	Applicability to SVE Sites
Correlation with Grain size Distribution Massman (1989)	- grain size distribution	- empirical constant	- Can be used to determine feasibility to SVE. Doesn't account for variable water content, bulk density, soil structure, or lateral heterogeneity of soils. Multiple measurements needed.
Correlation with Hydraulic Conductivity Massman (1989)	- water saturated hydraulic conductivity	- empirical constant	- Can be used to determine feasibility of SVE. Only valid for dry soils; doesn't account for "slippage" of gas by pore walls; or reduction of permeability by expandable clays. Multiple measurements needed.
Laboratory Determination Corey (1986)	- water flow rate - injected air pressure - soil porosity - cross-sectional area of sample		- Not applicable to SVE. Soil structure altered when placed in permeameter.
Air Injection Van Groenwoud (1968)	- injection of air flow rate - differential injection pressure - cross-sectional area tested		- Not applicable to SVE. Expands soil particles, increasing measured air permeability. Usually used to measure air permeability in surficial soils.

TABLE 1

AIR PERMEABILITY TEST METHODS  
(Continued)

Method Reference	Field or Lab Parameters	Assumed Parameters	Applicability to SVE Sites
Barometric Pressure Change  Weeks (1978)	- atmospheric pressure variation  - vertical extent of unsaturated zone	- viscosity of air	- Not applicable to SVE. Can only measure pressure differences if unsaturated zone is greater than 20m and has at least one layer with a permeability of 2 to 3 darcies. Large atmospheric fluctuations needed to measure permeability are unpredictable.
Pressure Buildup Test (gas well production test) Donohue and Ertekin (1982)	- well pressure - static reservoir pressure - gas flow rate - formation thickness - time at well shut-in - time interval during well shut-in	- viscosity of air - temperature of gas - compressibility factor	- Potentially applicable to determine SVE feasibility. Subsurface air pressure may not be high enough at SVE sites.
Pressure Drawdown Test (gas well production test) Donohue and Ertekin (1982)	- well pressure drawdown - static reservoir pressure - gas flow rate  - formation thickness - time of experiment - soil porosity - distance of monitoring well from extraction well	- gas compressibility - viscosity of gas  - temperature of gas	- Can be used to determine SVE feasibility and development of SVE design criteria. However Gas compressibility not important factor at SVE sites. Multiple measurements needed to account for lateral soil heterogeneity.

TABLE 1

AIR PERMEABILITY TEST METHODS  
(Continued)

Method Reference	Field or Lab Parameters	Assumed Parameters	Applicability to SVE Sites
Drawdown Curve (applied to drawdown test) Theis (1935)	<ul style="list-style-type: none"> <li>- extraction well flow rate</li> <li>- thickness of subsurface</li> <li>- time of experiment</li> <li>- pressure drawdown</li> <li>- distance between extraction well and monitoring wells</li> </ul>	<ul style="list-style-type: none"> <li>- viscosity of air</li> </ul>	<ul style="list-style-type: none"> <li>- Can be used to determine feasibility of SVE. Multiple monitoring well test measurements needed to account for lateral soil heterogeneity.</li> </ul>
Shell Method (developed for SVE) Johnson et al. (1990)	<ul style="list-style-type: none"> <li>- extraction well flow rate</li> <li>- monitoring well pressure</li> <li>- porosity of soil</li> <li>- atmospheric pressure</li> <li>- distance between extraction well and monitoring wells</li> <li>- time of experiment</li> </ul>	<ul style="list-style-type: none"> <li>- viscosity of air</li> </ul>	<ul style="list-style-type: none"> <li>- Can be used to determine SVE feasibility and development of SVE design criteria. Multiple monitoring well test measurements needed to account for lateral soil heterogeneity.</li> </ul>

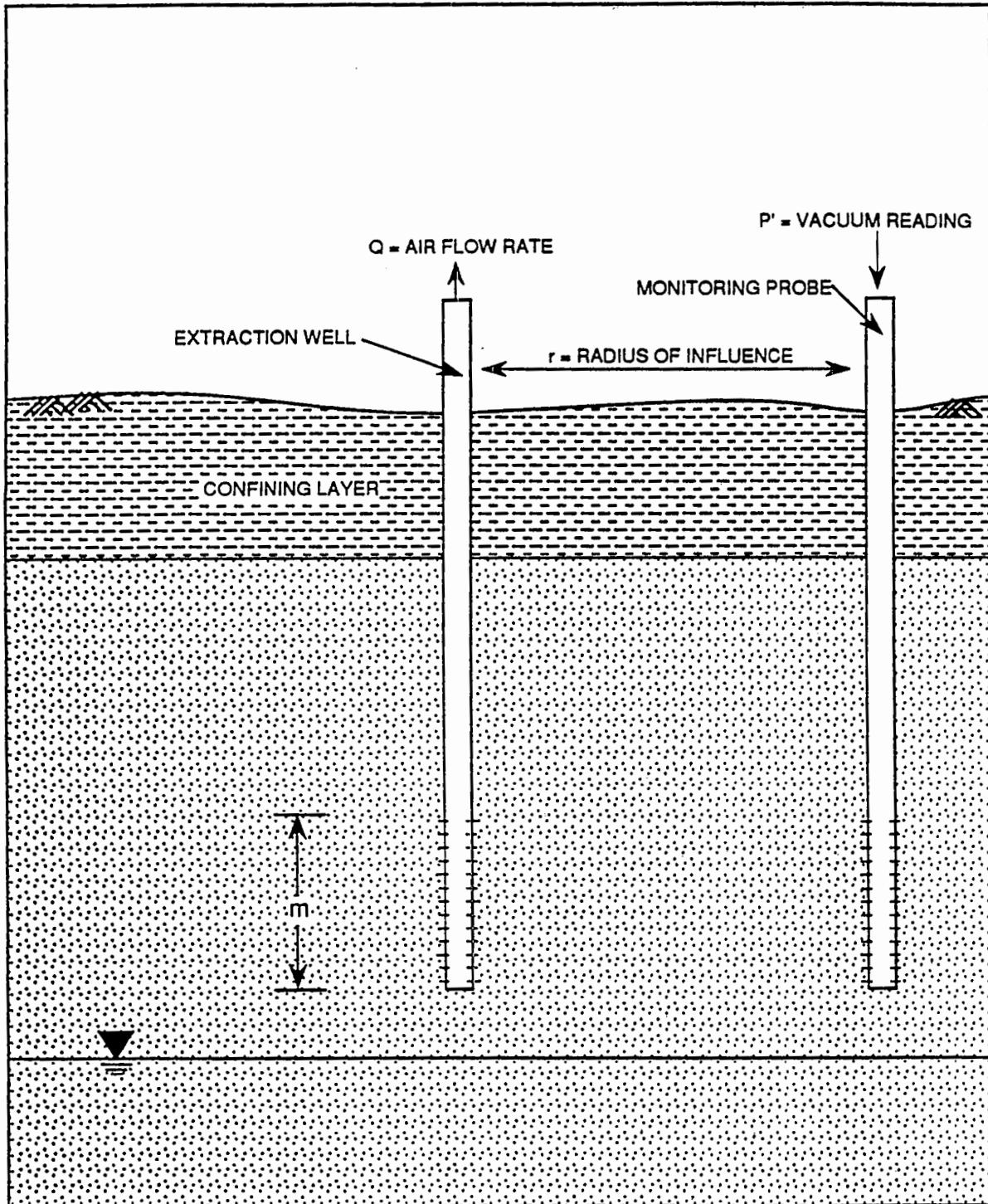


FIGURE 1 - AIR PERMEABILITY TEST COMPONENTS & MEASUREMENT PARAMETERS

# UNDERGROUND STORAGE TANKS CONTAINING HAZARDOUS CHEMICALS

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## ABSTRACT

The regulations issued by the United States Environmental Protection Agency (EPA) in 1988 require, with several exceptions, that underground storage tank systems containing petroleum fuels and hazardous chemicals be routinely tested for releases. This paper summarizes the release detection regulations for tank systems containing chemicals and gives a preliminary assessment of the approaches to release detection currently being used. To make this assessment, detailed discussions were conducted with providers and manufacturers of leak detection equipment and testing services, owners or operators of different types of chemical storage tank systems, and state and local regulators. While these discussions were limited to a small percentage of each type of organization, certain observations are sufficiently distinctive and important that they are reported for further investigation and evaluation. To make it clearer why certain approaches are being used, this paper also summarizes the types of chemicals being stored, the effectiveness of several leak detection testing systems, and the number and characteristics of the tank systems being used to store these products.

This paper has been reviewed in accordance with the U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

Federal underground storage tank regulations promulgated on 23 September 1988 establish a broad range of minimum requirements for the design, installation, operation and testing of a large fraction of tank systems in the United States. These regulations cover tank systems containing petroleum fuels as well as those containing other hazardous chemicals [1,2]. They are designed to help the underground storage tank community control and minimize the adverse environmental impact caused by leakage of product from a tank or its associated piping. The regulatory standards for leak detection in tank systems containing hazardous chemicals are more stringent than for those containing petroleum motor fuels. This paper describes (1) the

regulatory standards for leak detection in tank systems containing hazardous chemicals, (2) the types of chemicals being stored, (3) the types of containers in which these chemicals are stored, (4) the effectiveness of tank tightness tests and automatic tank gauging systems for detection of leaks in tanks containing chemicals other than petroleum, and (5) the approaches to leak detection being implemented by tank owners and operators. Because the first four items have been described in detail elsewhere [3-5], this paper simply summarizes them. The main focus is on the fifth item, specifically, the results of a preliminary survey of manufacturers of leak detection equipment for chemical tank systems, owners and operators of these systems, and state and federal regulators.

## REGULATORY STANDARDS

The federal regulatory standards for release detection in underground storage tanks issued by the EPA on 23 September 1988 [1] require that tank systems containing petroleum products and hazardous chemicals be tested periodically for releases. (A hazardous chemical is any substance defined by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [2].) The regulations for testing underground storage tanks containing hazardous substances are similar to those for tank systems containing petroleum products. During the first 10 years after the issuance of the regulations, all existing tank and pipeline systems containing hazardous substances must meet the requirements specified for tank systems containing petroleum products. After 10 years, all existing tank and pipeline systems must be upgraded, if necessary, to meet a more stringent set of requirements. These requirements emphasize the use of either double-wall tanks and piping or tanks and piping with secondary containment, both with interstitial monitoring to detect a leak in the inner wall of the system. These options are described in Section 280.42 (a) - (d) of the regulations [1]. If the tank system is new or has been upgraded, single-wall tanks and piping are permitted provided that owners and operators meet the following three criteria.

- Use any one of the release detection methods for tanks specified in Sections 280.43 (b) - (h) of the regulation or demonstrate to the implementing agency that an alternative method is at least as stringent. These include internal methods such as tank tightness testing systems, automatic tank gauging systems, and manual tank gauging for tanks 7,600 L (2,000 gal) or less, as well as external methods such as groundwater- and vapor-monitoring systems.
- Provide information to the implementing agency about health risks, effectiveness of corrective action, properties of the stored substance and characteristics of the site. If the health risks associated with the release of the chemical substance being stored are no higher than those associated with the release of a petroleum product, and there exist effective methods to clean up a release, then a single-wall tank system with release detection would be appropriate.

- Obtain approval from the implementing agency.

Although for some types of stored chemicals the single-wall tank system may be a highly effective way to satisfy the regulations, this option is treated as a variance. The onus is on the owner or operator to demonstrate to the implementing agency that the chemical substance will not be any worse than petroleum if accidentally released.

During the 10-year period between 1988 and 1998, the EPA regulations allow tank owners/operators to use either internal or external systems to test for releases. All systems attached to or inserted into the tank, piping, or interstitial space of double-wall tanks or piping are considered internal systems. Internal systems must meet a specific performance standard: they must have a capability to detect a leak of specific size with a probability of detection ( $P_D$ ) of 95% and a probability of false alarm ( $P_{FA}$ ) of 5%. No performance standards are specified for external systems, but specific requirements about conducting tests with such systems are given.

During this 10-year period, the regulation allows three general approaches to release detection, any of which might be practically pursued. The first two approaches use internal release detection systems and the third uses external monitoring systems. The first and most popular approach is to conduct an annual tank or line tightness test to detect small releases and to use more frequent monitoring by another method to detect large releases. All tank and line tightness tests must be performed at least once per year and must be able to detect leaks of 0.38 L/h (0.1 gal/h). In all cases where annual tightness tests are used, the regulation requires an additional form of leak detection in which tests on tanks are conducted at least monthly and those on pressurized lines at least hourly; this ensures the detection of excessively large releases. For tanks, daily inventory records must be reconciled monthly. For pressurized lines, leaks of 11.4 L/h (3 gal/h) must be reliably detected; this is usually accomplished by means of a mechanical line leak detector. The second approach is to install an automatic tank gauge or automatic line leak detector that is capable of detecting leaks of 0.76 L/h (0.2 gal/h); all monitoring tests must be done at least once per month. As with the tank and line tightness testing approach, this option also requires that there be a system for detecting large leaks. The tank gauge can be used to satisfy the inventory control requirements, and most automatic line leak detectors are designed so as to be able to satisfy the 11.4-L/h (3-gal/h) hourly test for pressurized piping. Interestingly, if the tank gauge is used to satisfy the "*Other*" option in the EPA regulation rather than the *Automatic Tank Gauge* option, inventory control is not required; however, owners or operators who use this option do so because of the potential for better and more accurate control of inventory. The third approach is to install an external monitoring system that can detect the presence of the stored chemical in or on the groundwater or in the backfill and soil surrounding

the tank system. Among other things, the success of external systems depends on the sensitivity of the sensor, the ability of the sensor to distinguish the stored chemical from other chemicals (i.e., its specificity), the ambient background noise level of the stored chemical, the migration properties of the chemical, and the sampling network. In many instances both internal and external methods are used in conjunction as a way to increase the probability of detection.

## STORAGE OF HAZARDOUS CHEMICALS

Two surveys were conducted to estimate (1) the number of tanks storing hazardous chemicals, (2) the types of stored chemicals by tank number and capacity and (3) the characteristics of the tanks by capacity, construction material, and age. A detailed description of these surveys can be found in [3,4].

The states participating in the program provided databases from their underground storage tank registration programs<sup>1</sup> for compilation and analysis; a total of 16 state databases were used in the analysis. The first survey, conducted in 1987, used data from the two largest states in terms of population, California and New York [3]. In the second survey, conducted in 1990, chemical tank data from New York and 13 other states were analyzed [4]. In selecting these states, efforts were made to obtain representative national coverage while simultaneously examining the more populous industrial states, which might be expected to have large numbers of chemical tanks. The 14 states included in the 1990 survey were Delaware, Florida, Illinois, Indiana, Maine, Massachusetts, Minnesota, New York, Missouri, Montana, Ohio, Texas, Virginia, and Wisconsin. New York was included in the second survey so that changes in its tank population since the earlier survey might be identified. Tables 1 through 5 summarize the results of the survey.

### TYPES OF CHEMICALS STORED

Solvents were found to comprise the single largest fraction of hazardous chemicals, comprising over 85% of the total. Table 1 presents the distribution of the most commonly stored chemicals by the number of tanks storing the chemical and by the total volume of product being stored. The 1987 data from New York and California are based only on the population of tanks containing *hazardous* chemicals, while the 1990 data from the 14 state databases are based on the population of all chemical tanks; the 1990 tabulation includes tanks containing *both* hazardous and nonhazardous chemicals. As illustrated in Table 1, acetone, toluene, xylene,

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<sup>1</sup> In 1984, as part of the amendments to the Resources Conservation and Recovery Act (RCRA), each state was required to register all underground storage tanks.

methanol and methyl ethyl ketone were found to be the most commonly stored chemical substances. The 1987 survey indicated that these five substances accounted for as much as 60% of all stored organic chemicals. After the fraction of tanks containing nonhazardous chemicals is removed from the 1990 databases, it can be shown that the five most common organics comprise 49% of all tanks containing hazardous chemicals, a figure that is slightly less than the estimate made from the survey of the two large states in 1987.

TABLE 1. SUMMARY OF THE MOST COMMONLY STORED ORGANIC CERCLA SOLVENTS

Chemical	1987 California Data		1987 New York Data		1990 Data (14 States)	
	% by Tank Number	% by Tank Volume	% by Tank Number	% by Tank Volume	% by Tank Number	% by Tank Volume
Acetone	22.8	18.0	12.0	18.3	3.9	4.2
Toluene	13.3	14.2	22.4	21.1	5.6	9.2
Xylene	8.1	6.3	15.5	11.7	---	2.5
Methanol	6.6	5.5	11.5	8.5	3.8	3.3
Methyl Ethyl Ketone	10.3	9.6	9.0	7.0	3.7	2.9
TOTALS	61.1	53.6	70.4	66.6	20.1	22.1

#### CHARACTERISTICS OF THE TANKS STORING CHEMICALS

Tables 2 through 5 give information about the characteristics of the tanks used to store chemicals. The characteristics tabulated are the number of tanks, the capacities of the tanks, the construction materials, and the ages of the tanks. Table 2 presents the total number of tanks compiled in the 1990 survey that contain hazardous substances. The 5,529 tanks containing hazardous chemicals represent approximately 57% of the 9,656 registered tanks containing products other than petroleum. The remaining statistics in the table (i.e., minimum, maximum, mean, and standard deviation) are based on a tabulation of the number of hazardous-substance tanks registered in each state. The mean number of tanks containing hazardous substances in each state is 395. The large standard deviation, the large difference between the mean and the median value, and the large spread between the states with the minimum and maximum number of tanks indicate that the number of tanks per state is quite variable. In comparison to the number of petroleum tanks, the number of tanks containing hazardous chemicals is only a very small fraction of the total underground storage tank population. Based on these data, the number of tanks containing hazardous materials throughout the United States should be between 1 to 2%

of the total tank population, whether calculated by number or by tank volume. The tabulation indicates that Illinois has more than twice the number of hazardous-substance tanks than any of the other states surveyed [4].

**TABLE 2. SUMMARY OF THE NUMBER OF TANKS CONTAINING HAZARDOUS CHEMICALS COMPILED FROM 14 STATE DATABASES\***

Statistics	Number of Tanks
Total for 14 States	5,529
Minimum	14
Maximum	2,060
Median	255
Mean per State	395
Standard Deviation	516

\*The total number of registered tanks containing nonpetroleum chemicals was 9,656.

Table 3 summarizes the capacities of the storage tanks containing hazardous substances, including the average volume of product. The percentage of tanks in each category (denoted in the first row across in Table 3) is based on the entire population of tanks containing hazardous chemicals. The statistics in the remaining rows, both percentages and average volumes, were computed from the average percentages and average volumes reported for each state. It is interesting to note that the states having the minimum, maximum, and median values vary considerably with tank capacity. Roughly 60% of the tanks in the state databases had capacities between 3,800 and 38,000 L (1,000 and 10,000 gal), with the average size of a tank (based on data from all states) being 7,205 gallons. Over 27% of the tanks are larger than 38,000 L (10,000 gal).

**TABLE 3. SUMMARY OF TANK SIZE DISTRIBUTIONS COMPILED FROM THE 14 STATE DATABASES AND EXPRESSED AS A PERCENTAGE OF THE NUMBER OF TANKS IN EACH STATE**

Statistical Parameters	Range of Tank Capacities (Gallons)					Average Volume
	< 1,000	1,000- <4,000	4,000- <10,000	10,000- <20,000	>20,000	
Total*	11.3	29.6	31.9	19.6	7.6	7,205**
Minimum	4.3	16.0	19.7	3.9	0.5	3,409
Maximum	44.7	39.9	37.6	24.6	29.6	101,293
Median	12.2	29.0	28.8	19.7	7.0	6,889
Mean*	13.7	27.9	29.6	18.2	9.2	7,555**
Standard Deviation	10.8	6.6	5.6	5.7	8.6	2,460

\* Totals for New York, Indiana, and Montana are based on CERCLA chemicals only.

\*\* Does not include the Delaware data because one of the tanks in that state has a capacity of 430,000 gal, and inclusion of these data would result in a misleading statistical estimate.

Table 4 summarizes the types of materials from which chemical tanks are constructed; the total is broken down according to the percentage of tanks constructed from steel, fiberglass-reinforced plastic, and "other" material. As was the case for tank size (Table 3), the percentage of tanks in each category (denoted in the the first row across in Table 4) is based on the entire population of tanks. The data indicate that 86% of the tanks are fabricated from steel and approximately 6% from fiberglass; about 4% are constructed of material(s) other than steel or fiberglass, and for another 4%, the construction material is not known.

**TABLE 4. SUMMARY OF TANK CONSTRUCTION MATERIALS COMPILED FROM LISTING OF REGISTERED TANKS IN THE 14 STATE DATABASES AND EXPRESSED AS A PERCENTAGE OF THE NUMBER OF TANKS IN EACH STATE\***

Statistical Parameters	Type of Construction Material			
	Steel	Fiberglass	Other	Unknown
Total	86.1	6.2	3.9	3.8
Minimum	62.9	0.0	1.5	0.0
Maximum	94.1	15.2	10.6	22.3
Median	83.9	6.6	5.6	2.6
Mean	82.4	7.1	5.1	6.4
Standard Deviation	8.9	4.6	2.6	7.6

\* Materials were not reported for Indiana, Minnesota, and Texas. Only steel tanks were reported for Montana. Values reported are percentages of the total tank populations in each state.

Table 5 summarizes the age of the tanks. The average percentages are based on the entire tank population. The remaining statistics are based upon the percentages reported for each state. Tank age was found to average 18 years, with approximately 40% of the tanks being more than 20 years old.

**TABLE 5. SUMMARY OF TANK AGE DISTRIBUTIONS COMPILED FROM 14 STATE DATABASES AND EXPRESSED AS A PERCENTAGE OF THE NUMBER OF CHEMICAL TANKS IN EACH STATE**

Statistical Parameters	Range of Tank Age (Years)				
	0 to 4	5 to 9	10 to 14	15 to 19	≥ 20
Average	4.9	16.2	21.6	17.6	39.7
Minimum	1.5	4.0	4.0	0.0	22.8
Maximum	22.2	23.0	26.1	25.6	86.7
Median	3.4	15.2	21.1	17.1	38.7
Mean	6.0	16.1	20.6	14.9	42.4
Standard Deviation	5.9	7.0	9.4	7.0	16.3

## CONSEQUENCES FOR RELEASE DETECTION

The results of these tabulations suggest that there is a strong potential for leakage from tanks containing hazardous substances. The statistics suggest that the tanks are generally old, made of steel, and fairly large. One would speculate that because the average age of these steel tanks is 18 years, many are unprotected by rust-resistant coatings and are highly susceptible to corrosion. As noted in the next section, the analysis performed in [5] suggests that most tank tightness and automatic tank gauging systems (which are internal leak detection systems) should be able to test these tanks effectively. Most of these leak detection systems were evaluated on 30,000- or 38,000-L (8,000- or 10,000-gal) tanks, which is consistent with the average capacity of tanks containing hazardous chemicals. Successful testing of chemical tanks should be possible, especially because their number is relatively small, approximately 1 to 2% of the total underground storage tank population. Moreover, a very small number of chemicals (five) accounts for roughly half of the hazardous substances being stored. External methods of leak detection can also be used provided that the leak detection system in question has the necessary specificity.

## VOLUMETRIC TANK TIGHTNESS TESTING

The same types of leak detection and monitoring systems used for testing tanks and pipeline systems containing petroleum products should be applicable to those containing chemicals provided that the sensors and equipment are compatible with the particular stored chemical and can be installed and used safely. The performance of these leak detection systems has, in most cases, been determined through an evaluation based on a single, specific, stored product. Volumetric leak detection systems, such as tank tightness testing systems and automatic tank gauges, were developed specifically to test storage tanks containing petroleum fuels, and any estimates of their performance, therefore, have been based on this class of liquids. Most performance evaluations of such systems have been conducted in 30,000- or 38,000-L (8,000- or 10,000-gal) tanks containing either gasoline or diesel fuels. If the tank contains a chemical that differs, in density, viscosity, or coefficient of thermal expansion, from the product used in the evaluation of a given leak detection system, the performance of that system when used to test a tank containing a nonpetroleum chemical will be different from what it was on the petroleum tank.

An analysis was made of the performance of tank tightness systems (and tank gauging systems) when applied to tanks containing chemicals other than petroleum fuels [5]. Since petroleum was the stored product in most evaluations of tightness testing systems, the analysis

attempted to determine impact of liquids with viscosities, densities, and thermal properties different from petroleum. The influence of the viscosity, the density, and the coefficient of thermal expansion on performance was investigated for the range of chemicals identified in the 14 state databases. The analysis examined the two most important sources of noise: thermal expansion or contraction of the product stored in the tank and the structural deformation of the tank resulting from any level or pressure changes before or during a test. Methods of compensating for thermal expansion/contraction and structural deformation were also investigated.

The analysis showed that (1) the performance of a volumetric leak detection system is directly proportional to the coefficient of thermal expansion of the product in the tank and (2) the waiting period required for the effects of structural deformation to subside is essentially the same for all values of density (even though higher densities produce greater deformation-induced volume changes immediately after any product-level change). When a leak detection system is used with a chemical product having a coefficient of thermal expansion higher than that of the product used in the evaluation of the system, the system's performance will be lower than it was in the evaluation. If the performance achieved in the evaluation barely meets the minimum standards established by the EPA, it is possible that the leak detection system will not meet the standard when used with chemicals having higher coefficients. Even if the leak detection system exceeds the minimum performance standards, it is possible that it will not meet the  $P_{FA}$  or  $P_D$  requirement; however, if a system has achieved high performance during the evaluation, judiciously changing the detection threshold can make it possible for the leak detection system to meet the requirements. Because gasoline has a higher coefficient of thermal expansion than many chemicals, a system evaluated with a gasoline product can be used with such chemicals and still maintain a similar level of performance.

This analysis did not examine volume changes due to evaporation and condensation, or those due to trapped vapor; the former may be an important source of error in tests conducted on underfilled tanks, and the latter an important source of error in tests conducted on overfilled tanks.

## **CURRENTLY USED APPROACHES TO LEAK DETECTION**

An informal survey of the owners and operators of chemical tanks, manufacturers of tank tightness testing and automatic tank gauging systems, and state and local environmental regulators was conducted by telephone to determine

- what methods of leak detection are being used for underground storage tanks (i.e., tanks and associated pipelines) storing hazardous substances,
- the basic characteristics of the chemical tank population to which these methods are applicable, and
- what inventory practices are being followed by owners/operators of underground storage tanks containing hazardous substances.

A questionnaire was prepared as a guideline to stimulate discussion. The questionnaire was designed to shed some light on what methods of leak detection are being applied to single-wall tanks between 1988 and 1998. The responses were given in confidence, and, as a result, the organizations discussing their environmental programs will not be disclosed by name. They are identified only by size and by a general description of the type of business they conduct. The organizations contacted ranged from small enterprises to large, well-known, Fortune 500 companies. The organizations that were interviewed were located in New York, California and Illinois.

Two surveys were planned, one to address leak detection practices and one to address inventory practices. In the initial survey, the survey taker started by contacting tank tightness testers and organizations that store chemicals to determine (1) which methods of leak detection are being used and (2) user perceptions as to the effectiveness of these methods. The second survey was designed to address the inventory practices of tank owners/operators and to collect 30 to 90 days of inventory records for analysis. As a check on the owners' responses, a brief discussion of inventory practices in the chemical industry was held with a major inventory/statistical inventory management service.

After the survey taker had contacted only a few organizations using tanks to store chemicals, it became clear that these organizations were either in the process of or had completed upgrading their systems to meet the regulatory standards required by 1998. As a consequence, the emphasis of the questions shifted from the technical details of the types of leak detection methods being used and the procedures followed for inventory reconciliation in single-wall tanks, and turned instead to the upgrading approaches. Instead of two separate surveys, only one was actually conducted.

## RESULTS OF DISCUSSIONS WITH TANK TESTERS

Three tank tightness testing services that are well known in the leak detection industry were asked whether they were capable of testing tanks containing chemicals other than petroleum and whether they had actually tested such tanks. At the time of the survey, all three companies had systems that conducted tests on overfilled tanks, and one had the ability to test partially filled tanks. (At present, all three firms have the capability to test partially filled tanks.)

All three said that they did test tanks containing chemicals. The only constraint on testing was that the temperature and level (volume) measurement systems inserted into the tank had to be compatible with the stored chemical. In general, such equipment was constructed of stainless steel and Teflon. All three firms indicated that up to 5% of their services involved testing tanks containing products other than petroleum. They all indicated that the performance of their systems was the same regardless of whether a tank contained petroleum or other chemicals. This response is consistent with our estimate of the number of tanks containing chemicals and our previous knowledge of this industry. None of the organizations manufacturing automatic tank gauges was contacted directly as part of this survey because, based on previous discussions with several automatic tank gauge manufacturers, it was expected that they would give the same general response as the tank tightness testing services. Automatic tank gauges are particularly suited for meeting regulatory requirements in tanks containing chemicals because tests can be conducted routinely and automatically without adding product to the tank.

## RESULTS OF DISCUSSIONS WITH TANK OWNERS AND OPERATORS

The survey taker contacted a total of 19 organizations that use chemicals in their operations and that own the tanks in which these chemicals are stored. He obtained responses from 13. The level of response varied considerably, as shown in Table 6, which summarizes the important aspects of the survey. Six of the firms, which are denoted by an asterisk, responded in sufficient detail to address all the questions prepared for the survey. A triple dash means that the organization did not respond to the question or did not know how to respond to the question.

In general, most firms had fewer than 50 tanks containing chemicals, and the median age of these tanks was approximately 20 years. Two of the firms did not indicate the number or age of their tanks because they were in the process of replacing all their single-wall tanks with aboveground tanks, double-wall tanks, or tanks with secondary containment. In all cases the tanks were used to store chemicals used in company operations. About half of the firms responded to the question of removal and disposal of the chemicals after the process had been completed. Waste chemicals were either reclaimed or stored in drums for removal.

None of the firms contacted indicated that they have had their tanks tested with a volumetric tank tightness testing system; one firm had its tanks tested with an air test, but this method was discontinued because of inaccuracy and other problems. (Air tests are no longer recommended, nor are they commonly used.) None of the companies contacted was using or planning to use automatic tank gauges for monitoring or inventory control purposes.

TABLE 6. SUMMARY OF IMPORTANT RESPONSES TO THE SURVEY

Company Product	Company Size	No. of Tanks	Mean Age	Was inventory control used?	Were tanks being replaced?	Were double-wall tanks being used?	Were aboveground tanks being used?	Were single-wall tanks with secondary containment being used?
Finishing*	Small	23	25+	Yes	Yes	Yes	---	---
Adhesives/Glues*	Medium	21	20	No	Yes	Yes	---	---
General Chemicals*	Large	17	20	Yes	Yes	Yes	When Possible	---
Adhesives/Glues*	Large	53	15-40	No	Yes	Yes	When Possible	---
Printing*	Medium	24	10	Yes	Yes	---	Yes	---
Computers*	Large	---	---	No	Yes	---	When Possible	Single-wall/vaulted
Chemicals	Small	11	15-	No	Yes	---	Yes	---
Cleaning Chemicals	Medium	21	20	No	Yes	---	---	---
Adhesives	Medium	24	25+	---	Yes	---	When Possible	---
General Chemicals	Large	13	---	---	Yes	---	Yes	---
Tank Farm	Medium	19	---	---	Yes	---	When Possible	---
Finishes/Paints	Medium	215	---	---	Yes	---	Yes	---
Computers	Large	---	---	No	Yes	---	Yes	---

\* Firms that answered all survey questions in detail.

Only three of the firms indicated that they kept inventory records, but these were for accounting and scheduling purposes only. These firms did not use inventory control data for leak detection. Based on the discussions with these three organizations, it was determined that the data being routinely obtained could not be used for inventory reconciliation either because there was no meter used to indicate the volume of material removed from the storage tank or the accuracy of this meter was inadequate for such an application.

All of the organizations contacted were replacing or planning to replace their single-wall tanks with either aboveground tanks or double-wall tanks with interstitial monitors. It was clear that the use of aboveground tanks was overwhelmingly preferred. The use of aboveground tanks permits visual inspection for leaks and facilitates maintenance; aboveground tanks also minimize the cleanup costs associated with an accidental leak.

## SUMMARY

Even though a diverse cross section of organizations was contacted, the responses obtained during the telephone survey should not be interpreted quantitatively; the number of organizations was very limited, and the survey was not statistically designed or statistically analyzed. As a consequence, the results should be interpreted cautiously, and the temptation to generalize, particularly about the status of regulatory compliance, should be avoided unless additional data are gathered. The following observations are noteworthy, however, either because the response was overwhelming or because it was ambiguous.

First, there is a strong tendency for owners/operators of tank systems to be planning ways to comply with the "upgraded standards" specified for 1998. There appears to be an emphasis on replacement of single-wall tank systems with (1) double-wall tanks and pipes equipped with interstitial monitors (and in some cases combined with external monitors also) or (2) tank systems mounted completely above ground so that visual inspection is possible. This emphasis on meeting the upgraded standards has occurred, we believe, because of the potential for serious environmental damage, the high clean-up costs, and the large liability associated with chemical contamination of the soil and groundwater. Concern may also stem from the fact that tanks containing chemicals are old (averaging 18 years) and constructed of steel (86%). What is not clear from the survey is how much time will be required for those organizations currently upgrading their tank systems to complete the process. If the time required for upgrading a tank system exceeds one year, the regulation requires that the tank system be tested by means of methods commonly used on tanks containing petroleum.

Second, none of the organizations contacted used inventory control as a means of leak detection. It also appears that this method of leak detection would be difficult to apply because of the lack of metering devices or the lack of accuracy in the metering devices being used. This observation was independently verified by a company that is heavily involved in analyzing inventory control data for owners or operators of chemical and petroleum tank systems.

Third, the tank testing firms contacted indicated that approximately 5% of their tests were conducted on tanks containing hazardous chemicals, a figure that is slightly higher than the estimated percentage of such tanks in existence in the U.S. This is inconsistent with the response obtained from the 13 tank-owning organizations that responded to the survey. None of these organizations indicated that they used such services. In addition, the tank testing firms did not know whether the owners and operators of the tanks they tested employed monthly inventory reconciliation. (Inventory reconciliation is required by the regulations when the only form of

leak detection is an annual tightness test.) The contradictory responses offered by the testing firms and the owners and operators of tank systems containing chemicals suggest that the owners/operators who responded to the survey may not be representative of the entire chemical tank community.

Fourth, additional information is required before any assessment can be made of release detection practices in effect now and during the next eight years (the time allowed for owners/operators of chemical storage tanks to upgrade their systems in anticipation of the 1998 EPA deadline).

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**SUBSURFACE FATE AND TRANSPORT OF PETROLEUM HYDROCARBONS**  
**FROM LEAKING UNDERGROUND STORAGE TANKS:**  
**A BASIS FOR EVALUATING THE EFFECTIVENESS OF CORRECTIVE ACTIONS**

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**ABSTRACT**

The problems associated with leakage of motor fuels and organic chemicals from underground storage tanks (USTs) are compounded by a general lack of understanding of the partitioning, retention, transformation, and transport of these contaminants in the subsurface environment. The research material developed in this project is the result of an intensive data collection and evaluation effort that compiled a very broad range of knowledge of contaminant behavior in the subsurface into a single document. The document describes micro-scale fate and transport processes of contaminants in the subsurface as a means to understanding their larger scale movement. This, in turn, leads to a more thorough understanding of the application of corrective measures and remediation techniques. The micro-scale analysis focuses on 13 loci, each of which represents a location and condition in the subsurface environment where contaminants may exist after an UST release.

This technical handbook is a data base of scientific knowledge that can be drawn upon by environmental scientists, engineers, and managers of varying levels of technical expertise to define the key parameters and to increase the level of sophistication in the approach to the problem of motor fuel leaks from USTs. It serves to strengthen an understanding of the fate and transport processes vital to effective remediation, and it serves as a source book of information, data, and equations to support more quantitative assessments of pollutant fate and transport processes associated with different remedial technologies.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

### BACKGROUND

The U.S. Environmental Protection Agency (EPA) has developed a comprehensive program for regulating certain underground storage tanks (UST) that contain regulated substances. With this program comes the need for development of guidance to assist those parties involved in complying with regulatory requirements. One significant portion of the legislation that has been developed pertains to corrective actions for releases of petroleum products such as gasoline and other motor fuels. EPA estimates that over 95 percent of the estimated 1.4 million UST systems are used to store petroleum products.

Current regulations require that owners and operators take corrective measures to mitigate releases from underground storage tanks. To date, guidance documents developed by the EPA and other organizations present various technologies applicable to remediation of the subsurface environment. However, only minimal amounts of information have been generated with regard to evaluating the movement and disposition of motor fuel contaminants in the subsurface environment, and only recently has significant research been devoted to this effort. Currently, investigators have no guidance available to evaluate corrective actions at UST sites that is based upon the scientific principles governing the behavior and degradation of motor fuel constituents in the subsurface environment. Recognizing this, EPA sponsored the comprehensive, scientific literature research effort resulting in a handbook-style resource document.

The primary focus of this project was to formulate a data base of comprehensive scientific knowledge that can be drawn upon to define the key parameters and to increase the level of sophistication in the approach to the problem of motor fuel leaks from USTs. The focus on organic contaminants is based on the reality that over 95 percent of materials stored in underground tanks is some type of petroleum product. As a starting point, EPA sponsored a two-day seminar where recognized experts and specialists in eight specific disciplines presented information on the physical, chemical, and biological properties, and fundamentals of motor fuel and organic chemical behavior in the subsurface environment. Based on the information presented at this seminar, an evaluation of available scientific data was conducted to provide a comprehensive, up-to-date understanding of the physical and chemical "rules" governing contaminant fate and persistence in the subsurface environment.

### OBJECTIVES OF HANDBOOK

The EPA's Office of Underground Storage Tanks (OUST) is responsible for establishing the Agency's regulatory program for managing underground storage tanks. The Risk Reduction Engineering Laboratory (RREL) of EPA's Office of Research and Development is responsible for providing engineering and scientific support to OUST. One means of providing this technical support is through the preparation of guidance materials such as handbooks,

manuals, and technical reports. To date, there have been a number of such documents developed by the EPA and other organizations on various aspects of the UST corrective action process. A review of these and other currently available documents indicated that there was no pre-existing guidance which directly relates fate and transport processes to corrective actions, a shortcoming deemed serious by EPA.

Therefore, the primary objective of this handbook was to provide a comprehensive, in-depth research report with detailed coverage of fate and transport mechanisms that also includes timely discussion of these mechanisms as they relate to currently used or innovative approaches to UST releases. The handbook is intended to benefit environmental scientists, engineers and managers of varying technical expertise by increasing the level of sophistication in the approach to the problem of motor fuel leaking from USTs. It is also intended to serve as a source book of information, data, and equations, to support quantitative assessments of pollutant fate and transport.

To further support timely and technically sound responses to leaking USTs, the information in this handbook provided the technical basis for the preparation of the desired guidance handbooks recently released by HWERL:

- o ASSESSING UST CORRECTIVE ACTION TECHNOLOGIES: Site Assessment and Selection of Unsaturated Zone Treatment Technologies. Report No. EPA/600/2-90/011, Risk Reduction Engineering Laboratory, Cincinnati, OH, March 1990.
- o ASSESSING UST CORRECTIVE ACTION TECHNOLOGIES: Early Screening of Clean-up Technologies for the Saturated Zone Report. No. EPA/600/2-90/027, Risk Reduction Engineering Laboratory, Cincinnati, OH, June 1990.

#### RESEARCH APPROACH

As a starting point, EPA sponsored a two-day seminar where recognized experts and specialists in eight specific disciplines presented information on the physical, chemical, and biological properties and fundamentals of motor fuel and organic chemical behavior in the subsurface environment. Based on the information presented at this seminar, a concept was developed that a substance leaking from an UST will be present in and transient between one or more locations or settings in the subsurface environment. A total of 13 of these locations, referred to as physicochemical-phase loci, were identified as the focal points for this research report. Each of the 13 loci represents a point in space (or location) and the physical state of the leaked substance that together describe where and how these contaminants may exist in the subsurface environment after an UST release. For example, contaminants may be dispersed as a component of soil gas, or they may be dissolved in the water film surrounding a wet soil particle in the unsaturated zone. These are just two examples of the 13 loci. Collectively, the 13 loci represent all locations/states where and how leaked material may be present in the subsurface environment. The distribution of contaminants among these loci is constantly changing, as

contaminants tend to move between different loci at varying rates over time. Table 1 presents a brief description of each locus. Figure 1 presents a schematic cross-section of the subsurface environment and identifies where each locus may exist in terms of the unsaturated and saturated zones.

These 13 loci can be used in reference to any type of contaminant that enters the subsurface environment. However, for the purpose of this research effort, the contaminants of interest are petroleum products (e.g., gasoline) constituents, i.e., hydrocarbons and other chemicals, including common gasoline additives. As pointed out previously, the reason for focusing on petroleum product constituents is that these products make up over 95 percent of the materials managed in underground storage tanks. All references to contaminants in this handbook are, therefore, with regard to hydrocarbons and associated organics.

The ultimate objective in conducting research on the fate and transport of hydrocarbons in the manner presented, i.e., locus by locus, and process by process from a micro-scale perspective, is to gain a better understanding of the basis for larger scale contaminant movement. The ways in which the behavior of hydrocarbons may be altered are directly related to remediation techniques. Therefore, a comprehensive understanding of the fundamental "rules" of contaminant behavior engenders a better understanding of how this behavior may be induced or prohibited to optimize a given remedial strategy.

Each locus, after being initially defined, was researched and evaluated in terms of the mobilization, immobilization, transformation, and bulk transport processes that pertain to it, and in terms of how these various processes affect the locus. Table 2 identifies the different processes that were considered when evaluating each locus. In general, many, but not all of these processes apply to a given locus. There are also many processes which are important to more than one locus. Because of this, it was necessary to minimize redundancy in the material presented. To accomplish this, detailed discussion of a given process is usually limited to a single locus section - that for which the process is of particular importance or to which it most appropriately belongs. In other loci sections where the process is discussed, the reader is directed to the section(s) containing detailed discussions rather than repeat the material.

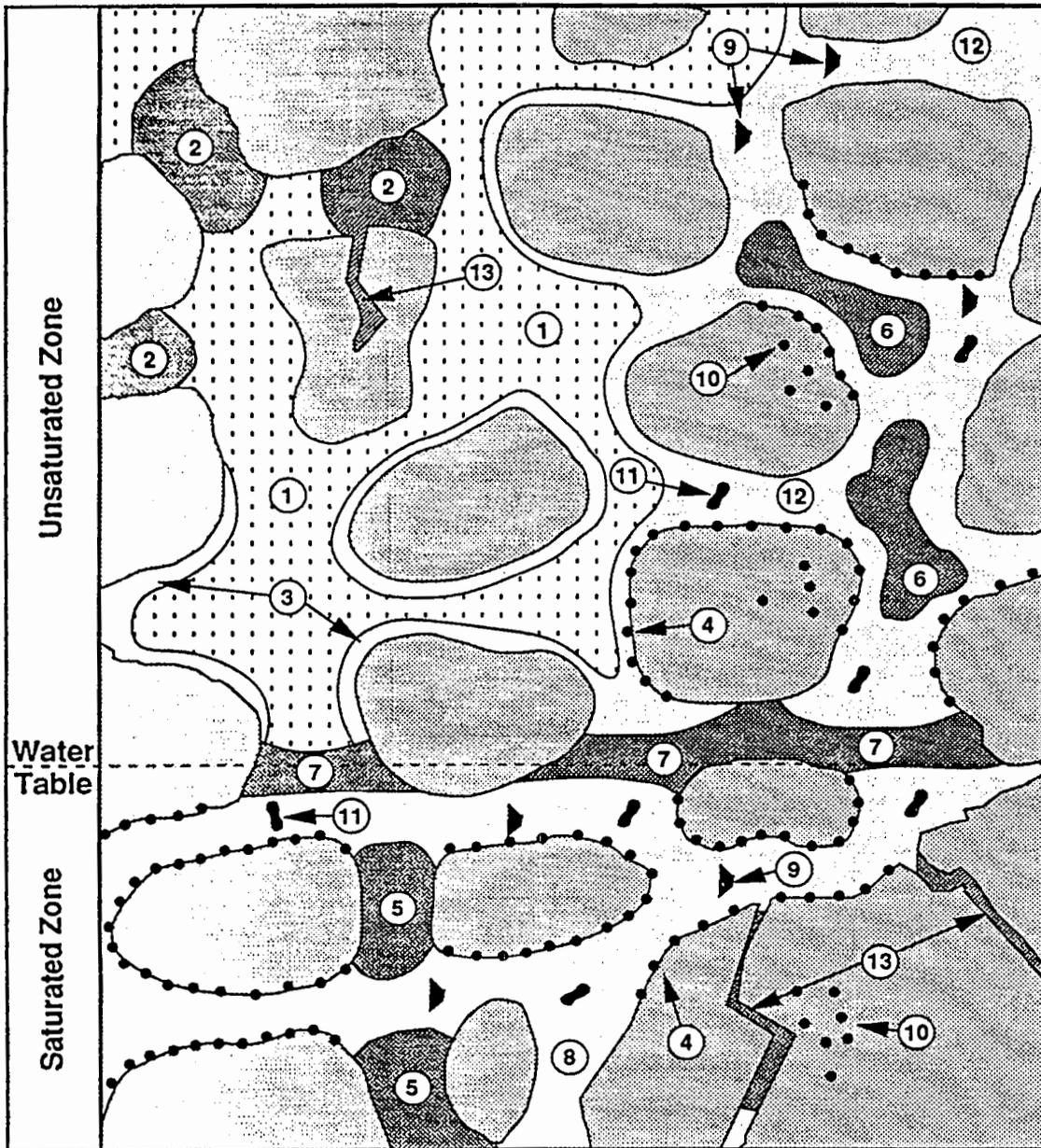
The one locus that is treated differently from others in the handbook is locus no. 11 (contaminants sorbed into/onto biota). It is treated differently in terms of section organization and contents because locus no. 11 is considered to be a transformation process in itself, i.e., it is considered to be both a locus and a process.

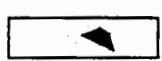
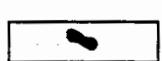
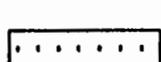
Following discussions of partitioning, transformation, and transport processes, each handbook section provides guidance on calculating maximum and average values for the contaminant storage capacity of the locus, including estimation of parameter values and example calculations. In addition, example calculations are provided where appropriate for mass transport processes (e.g., advection, dispersion, and diffusion) and partitioning equilibrium processes (e.g., calculations for dissolution and adsorption). Lastly, the relative importance of each locus with regard to

TABLE 1

BRIEF DESCRIPTIONS OF THE THIRTEEN  
PHYSICOCHEMICAL-PHASE LOCI

Locus Number	Description
1	Contaminant vapors as a component of soil gas in the unsaturated zone.
2	Liquid contaminants adhering to "water-dry" soil particles in the unsaturated zone.
3	Contaminants dissolved in the water film surrounding soil particles in the unsaturated zone.
4	Contaminants sorbed to "water-wet" soil particles or rock surface (after migrating through the water) in either the unsaturated or saturated zone.
5	Liquid contaminants in the pore spaces between soil particles in the saturated zone.
6	Liquid contaminants in the pore spaces between soil particles in the unsaturated zone.
7	Liquid contaminants floating on the groundwater table.
8	Contaminants dissolved in groundwater (i.e., water in the saturated zone).
9	Contaminants sorbed onto colloidal particles in water in either the unsaturated or saturated zone.
10	Contaminants that have diffused into mineral grains or rocks in either the unsaturated or saturated zone.
11	Contaminants sorbed onto or into soil microbiota in either the unsaturated or saturated zone.
12	Contaminants dissolved in the mobile pore water of the unsaturated zone.
13	Liquid contaminants in rock fractures in either the unsaturated or saturated zone.



- |   |                                       |   |  |
|---|---------------------------------------|---|--|
|  | SOIL PARTICLES OR ROCK                |  | CONTAMINANTS SORBED ON SOIL OR<br>DIFFUSED INTO MINERAL GRAINS |
|  | LIQUID CONTAMINANT<br>(Organic Phase) |  | MOBILE COLLOIDAL PARTICLES<br>WITH SORBED CONTAMINANT          |
|  | WATER WITH DISSOLVED<br>CONTAMINANT   |  | SOIL MICROBIOTA WITH<br>SORBED CONTAMINANT                     |
|  | SOIL AIR WITH<br>CONTAMINANT VAPORS   |  | LOCI NUMBER (SEE TABLE 1)                                      |

This is a highly schematic representation of the 13 loci outlined in Table 1 as they exist in the subsurface. A more detailed explanation of each locus is presented in the text.

**Figure 1. Locations of Loci in Terms of Unsaturated and Saturated Zones**

TABLE 2

## FATE AND TRANSPORT PROCESSES CONSIDERED IN EVALUATING EACH LOCUS

Partitioning and Transformation Processes	Bulk Transport Processes
<u>Partitioning</u>	
Dissolution of Liquid Contaminant into Water	Advection/Dispersion of "Water-Wet"* Liquid Contaminants
Volatilization of Liquid Contaminant into Soil Air	Advection/Dispersion of "Oil-Wet"** Liquid Contaminants
Sorption of Liquid Contaminant onto "Dry" Soil	Advection/Dispersion of Liquid or Aqueous Phase Contaminants in the Unsaturated Zone
Partitioning between Aqueous and Vapor Phases	Advection/Dispersion of Liquid or Aqueous Phase Contaminants in the Saturated Zone
Sorption of Aqueous Phase Contaminants to Soil	Advection/Dispersion of Contaminants in Soil Air
Condensation of Vapor Phase Contaminants on Dry Soil	Transport with Water of Contaminants Attached to Biota or Colloidal Particles
<u>Transformation</u>	
Chemical Oxidation of Contaminants	Diffusion of Contaminants in Liquids
Biodegradation of Contaminants	Diffusion of Contaminants in Solids

\* "Water-wet" refers to the condition where water preferentially (vs petroleum products) wets the surface of the soil particles.

\*\* "Oil-wet" refers to the condition where the petroleum product preferentially wets the surface of the soil particles.

fate and transport of contaminants is discussed in terms of remediation, interaction with other loci, identification of critical information gaps, and recommendations for future research.

Even though remediation is not the subject of this handbook, indirectly the ultimate purpose of conducting the loci research is to increase the sophistication of current approaches to site assessment and corrective action selection. Brief discussions of remediation and corrective measures are presented in each locus section in three places; in each introductory subsection, in the subsections discussing effective partitioning processes, and in the overview of each locus' relative importance presented in the last subsection.

#### ORGANIZATION OF HANDBOOK

The main body of the handbook is organized into 13 major sections, one for each locus. Each section, except for Section 11 (locus no. 11), consists of the same five main subsections, which, in turn, contain discussions that are presented similarly. As previously explained, locus no. 11 is dealt with differently in terms of the structure of its section because of its nature, i.e., it is both a locus (biota) and a process (biodegradation). Table 3 presents a generic outline of the locus sections. Although many sections deviate slightly from the standard outline, the same types of information and evaluations have been included in all sections. Brief descriptions of some of the major headings of Table 3 are presented below.

The title of Section X.1 is self explanatory. Section X.2 discusses in detail the fate and transport mechanisms affecting the locus. The text is interspersed with discussion of how these mechanisms relate to corrective measures and how they could be enhanced to support remediation. Section X.2.2 describes the processes governing contaminant transport, either as mass movement of the locus (advection/dispersion) or as mass transformation to other loci (dissolution/volatilization/condensation/sorption). Section X.2.3 discusses the mechanisms that influence fixation of the locus by: 1) enhancing phase exchange or mass transport out of the locus into another less mobile locus, or 2) fixing the locus as a whole, for possible future remediation or as a permanent corrective action. Section X.2.4 discusses transformation that can potentially act on the locus to produce physical and/or chemical changes, which in turn result in a less complex, less toxic residual. Among the transformation processes are biodegradation, chemical oxidation, hydrolysis, elimination, dehydrogenation and redox reactions.

Section X.3 describes methods for quantifying the mass of contaminant existing in the locus, i.e., storage capacity. A typical section presents the factors influencing storage capacity and equations to calculate storage capacity. Guidance is provided on inputs for calculating average and maximum storage capacity. Sources of data for the various parameters required in the calculations are cited, many of which are found within the text.

TABLE 3. GENERIC OUTLINE FOR LOCUS SECTIONS

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SECTION X - LOCUS NO. X

- X.1 Locus Description
  - X.1.1 Short Definition
  - X.1.2 Expanded Definition and Comments
- X.2 Evaluation of Criteria for Remediation
  - X.2.1 Introduction
  - X.2.2 Mobilization/Remobilization
  - X.2.3 Fixation
  - X.2.4 Transformation
- X.3 Storage Capacity in Locus
  - X.3.1 Introduction and Basic Equations
  - X.3.2 Guidance on Inputs for, and Calculation of, Maximum Value
  - X.3.3 Guidance on Inputs for, and Calculation of, Average Value
- X.4 Example Calculations
  - X.4.1 Storage Capacity Calculations
  - X.4.2 Transport Rate Calculations
- X.5 Summary of Relative Importance of Locus
  - X.5.1 Remediation
  - X.5.2 Loci Interactions
  - X.5.3 Information Gaps

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In Section X.4, example calculations of storage capacity within the locus and other important processes defined by equations within the text (e.g., transport velocity, dissolution rate, etc.) are worked out. The examples employ hypothetical site conditions and contaminant characteristics that might reasonably be encountered in the field to convey a realistic sense of locus behavior in the subsurface.

Finally, Section X.5 evaluates the locus in terms of its overall impact in the subsurface and its relation to other loci. Among the factors considered are mass of the locus relative to total contaminant mass, locus impact on and transfer to other loci, and the degree to which corrective action measures can be effectively employed. Also discussed in Section X.5 is the availability of data on the locus in terms of completeness of research conducted and information gaps needing to be filled to better understand the locus.

THE INCINERATION OF LEAD-CONTAMINATED SOIL  
RELATED TO THE COMPREHENSIVE ENVIRONMENTAL RESPONSE  
COMPENSATION AND LIABILITY ACT (CERCLA) (SUPERFUND)

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ABSTRACT

The fate of lead on incinerated CERCLA soil was evaluated at the USEPA Incineration Research Facility (IRF) at Jefferson, Arkansas. This facility houses a pilot-scale rotary kiln incinerator which was fed lead contaminated soil for the reported study. The analytical results indicate that lead emissions to the atmosphere after the air pollution control device (APCD) remained constant at about 7 percent of the lead content in the feed at 816°C (1500°F) and 100 percent excess air. When the excess air was reduced to 50 percent, the emissions ranged from 6 to 9 percent of the lead content in the feed at 816°C (1500°F).

INTRODUCTION

One of the primary purposes of the Incineration Research Facility (IRF) in Jefferson, Arkansas, is to support the Environmental Protection Agency (EPA) Regional Offices and the Office of Solid Waste and Emergency Response in evaluation of incineration as a disposal option for the remediation actions at Superfund sites. A priority site that fell into this category was the Baird and McGuire location at Holbrook, Massachusetts, which is located in EPA Region I. Region I requested that the contaminated soil from this location be burned to generate data that could be used for the evaluation of incineration as a treatment at this Superfund site. Incineration was proposed to destroy the pesticides (pp'-DDT, pp'-DDD, pp'-DDE and Methoxychlor), but the fate of the metals, lead and arsenic, in the soil was also of concern both during and after incineration. In addition to the destruction of organics, the mission of the test was to evaluate the different operating conditions and how they would impact the distribution of the lead and arsenic to the various residual streams. This paper reports the partitioning to the incinerator discharge streams: ash, scrubber water and flue gas.

The experimental work was conducted at the USEPA Incineration Research Facility (IRF) (1). The rotary kiln incineration system (RKS) was selected for this research, with the ionizing wet scrubber as the air pollution control device. The design characteristics of the kiln system and the ionizing wet scrubber are:

#### Main Chamber

Length, outside	2.61 m (8 ft - 7 in.)
Diameter, outside	1.22 m (4 ft)
Length, inside	2.44 m (8 ft)
Diameter, inside	0.95 m (3 ft - 1-1/2 in.)
Chamber volume	1.74 m <sup>3</sup> (61.4 ft <sup>3</sup> )
Construction	0.63 cm (0.25 in.) thick cold-rolled steel.
Refractory	12.7 cm (5 in.) thick high alumina castable refractory, variable depth to produce a frustroconical effect for moving solids.
Rotation	Clockwise or counterclockwise 0.2 to 1.5 rpm
Solids retention time	1 hr (at 0.2 rpm)
Burner	North American Burner, rated at 770 kW (2.6 MMBtu/hr) with liquid feed capability.
Primary fuel	Natural Gas
Feed System	
Liquids	Positive displacement pump via water-cooled lance.
Sludges	Moyno pump via front face, water-cooled lance.
Solids	Metered twin-auger screw feeder or fiber pack ram feeder.
Temperature (max)	1010°C (1850°F)

#### Characteristics of the Afterburner Chamber

Length, outside	3.05 m (10 ft)
Diameter, outside	1.22 m (4 ft)
Length, inside	2.74 m (9 ft)
Diameter, inside	0.91 m (3 ft)
Chamber volume	1.80 m <sup>3</sup> (63.6 ft <sup>3</sup> )
Construction	0.63 cm (0.25 in.) thick cold rolled steel
Refractory	15.24 cm (6 in.) thick alumina castable refractory
Gas residence time	1.2 to 2.5 sec depending on temperature and excess air
Burner	North American burner rated at 590 kW (2.0 MMBtu/hr) with liquid feed capability
Primary fuel	Natural gas
Temperature	1200°C (2200°F)

#### Characteristics of the Ionizing Wet Scrubber APCD

System capacity	85 m <sup>3</sup> /min (3000 acfm) at 78°C (172°F) and 101 kPa
inlet gas flow	(14.7 psia)
Pressure drop	1.5 kPa (6 in. wc)
Liquid flow	15.1 L/min (4 gpm) at 345 kPa (50 psig)
pH control	Feedback control by NaOH solution addition

## MUFFLE FURNACE EXPERIMENTATION

Prior to the start of the parametric incineration study on the Baird and McGuire soil, a series of waste composition/leachability tests were conducted with the soil in a laboratory-size muffle furnace to determine the optimum experimental conditions that might be used for the soil incineration tests. The muffle furnace tests consisted of nine experiments during which various concentrations of lead in the contaminated soil were heated at 982°C (1800°F) for one hour. The weight loss (moisture and volatiles) were determined for each sample and the resulting ash was analyzed for total lead (Pb). Uncontaminated clay was mixed with the soil to get variable lead concentrations in the feed. Toxicity Characteristic Leaching Procedure (TCLP) samples of the feed as well as the ash were also taken and analyzed for lead and compared with the total waste/ash analysis. Two percent lime by weight was added to one of the samples and two percent alum (ferric ammonium sulfate,  $\text{FeNH}_4(\text{SO}_4)_2$ ) was added to another of the samples to determine if these additives affected the distribution of metals in the ash.

## INCINERATOR TESTING

A series of five tests were performed using the RKS at the IRF to determine the relative partitioning of lead to the different waste streams. This was a part of the testing series to establish that incineration could effectively destroy the organic contaminants in the soil and to document the fate of lead distributions as a function of incineration conditions.

The test variables were kiln temperature and oxygen at the kiln outlet. Kiln temperature was targeted for 816 and 982°C (1500 and 1800°F) and the oxygen concentration at the kiln exit flue was targeted at 7 and 10 percent, (50 percent and 100 percent excess air.)

All the soil was fed to the kiln in fiber-pack drums via the RKS ram feeder system. The fiber-packs, each of which contained about 5.0 kg (11 lb) of soil, were fed at the rate of one every 5 minutes resulting in a feed rate of 60 kg/hr (132 lbs/hr). The kiln rotation was set to give a nominal solids residence time of 0.5 hr.

## SAMPLES

The samples taken during each test were:

1. Scrubber blowdown water for lead (grab sample),
2. Feed and kiln ash for total lead analysis (grab sample),
3.  $\text{O}_2$  concentrations at kiln outlet (continuous analyzer),
4. Stack gas particulate matter, lead and POHCs.
5. Feed and ash for TCLP determinations for lead.
6. Scrubber water for TCLP.

## TEST RESULTS AND DISCUSSION

### MUFFLE FURNACE TEST RESULTS

Baird and McGuire soils with varying concentrations of lead were heated in the muffle furnace at nominal conditions to determine the effect of lead feed concentration on the resultant lead ash concentration and leachability. TCLP leachates of the feeds and ashes were analyzed for lead to observe the effects on lead mobility.

The test results are summarized in Table 1. These data show the various concentrations of lead which were derived by mixing the contaminated soil, which contained 45 mg/kg of lead with uncontaminated clay.

As the concentration of lead decreased, the data suggest that an initial lead concentration of 45 mg/kg or less will always have less than 0.05 mg/L TCLP in this matrix and would be well below the guidance level of 5 mg/L for the ash. The muffle furnace tests on the original soil with a concentration of 45 mg/kg of lead had an ash content containing 5.1 mg/kg lead, and a TCLP of <0.05 mg. As the concentration of soil in the mixture (lead in the mixture) was lowered, the TCLP remained at <0.05 mg/L despite variations of lead concentrations of up to 5.8 in the ash.

When 2 percent lime was added to the 100 percent soil (one data point), the lead concentration was 44 mg/kg. After testing in the muffle furnace, the lead concentration was 6.9 mg/kg in the ash. This was an increase in the retention of lead in the ash compared to the 5.1 mg/kg retention in the untreated soil sample and the TCLP was still <0.05 mg/L.

The addition of 2 percent alum to the 100 percent soil increased the lead content of the ash to 7.4 mg/kg. This one point determination suggests that alum would be an addition to a lead contaminated soil that would increase the retention of the lead in the ash.

### Incineration Test Results

Five incineration tests were conducted on the contaminated soil from the Baird and McGuire site. The lead concentration of the soil received was not adjusted as it was for the muffle furnace tests however the lead concentration varied from 16 to 27 mg/kg. Table 2 presents a summary of the test conditions and the concentrations of incinerator variables measured during the tests.

The test results in Table 2 show the conditions of operation. Tests 1, 2 and 5 had target temperatures of 816°C (1500°F). A mean average of the temperatures achieved for these three tests were 832°C (1530°F), 839°C (1540°F) and 844°C (1551°F). Tests 3 and 4 had a target temperature of 982°C (1800°F) and operated at 994°C (1821°F) for both tests. Temperatures for all the tests were close to the target conditions, and operating temperatures were judged successful. For ease of presentation, the temperatures 816°C (1500°F) will be used for Tests 1, 2, and 5, and 982°C (1800°F) will be used for Tests 3 and 4.

The mean experimental oxygen concentrations achieved in Tests 1, 3 and 5 were 11.3 percent, 10.4 percent and 11.2 percent. Tests 2 and 4 were at 7 percent and achieved concentrations of 6.8 percent and 7.5 percent.

The resulting distributions of lead in the ash kiln exit gases and scrubber water are contained in Table 3. The ash generation rate was determined by using the feed rate less the volatiles and moisture. This table has been arranged by temperature of operation. Tests 1, 2 and 5 are the 816°C (1500°F) and Tests 3 and 4 are the 982°C (1800°F) operating condition. Test 5 was a duplicate of Test 1 to check the analytical data precision.

On the basis of lead retention in the ash, incinerating at 816°C (1500°F), at 50 percent excess air (Test 2) appeared to give the best operating condition of the five tests (Figure 1). The retention of the lead in the ash was 151 percent of the lead feed based on the amount of lead/hr in the ash versus the feed. The emissions to the atmosphere were 5.7 percent of the feed (Figure 2). Considering the scrubber waste catches 4.3 percent of the lead feed and the emissions to the atmosphere 5.7 percent, then the total emissions before the ionized wet scrubber were 10 percent of the feed (Figure 3). Operating the incinerator at the lower temperature and lower oxygen rate increased the retention of the lead in the ash and reduced the emissions to the atmosphere.

Operation at 816°C (1500°F) and 11 percent oxygen was the second best operating condition that partitioned lead to the ash. The lead retained in the ash (Tests 1 and 5) averaged 11.4 percent. Atmospheric lead emissions were 7.1 percent of the feed lead. If the lead emissions to the atmosphere are the important consideration, rather than retention in the ash, then high air flow, 11 percent (100 percent excess air) is the better condition operation. However, the total emissions were 11.5 percent before the abatement system, indicating that if the air pollution abatement system operated at the same efficiency at both the higher and lower temperature of operation, then this was not the best condition of operation.

Incinerating the soil at 982°C (1800°F) indicated that retention of lead in the ash was almost the same at both oxygen concentrations; 7 percent oxygen resulted in 34 percent lead retention in the ash and 11 percent oxygen resulted in 33 percent retention in the ash. The lead emissions were 8.9 percent of the feed at 7 percent oxygen concentration and 6.7 percent at 11 percent oxygen concentration.

The feed and ash, in all tests, had a TCLP value of less than 0.05 mg/L (the detection limit). A more practical method for summarizing the data for lead retention in the ash is by decreasing the calculated lead input of the soil by the scrubber water lead content and the emissions. This indicates that the ash retention averaged 89 percent of the lead input at 816°C (1500°F) operating temperature and 83 percent at 982°C (1800°F). These figures do not change the conclusions made from the analytical results, but it does reduce the lead retention results of over 100 percent in the ash.

The data which indicate that lead is retained in the ash in excess of 100 percent are in line with pilot scale and full scale data previously obtained for lead. Emissions of lead from sewage sludge incineration range from less than 1 percent to 20 percent; the 20 percent being when no pollution control system was used (3).

The EPA Superfund Innovative Technology Evaluation (SITE) program (4) tested an innovative incineration system where 18 incineration tests with a feed containing lead were performed. The operating temperatures and oxygen were varied similar to the test conditions reported in this paper (4). Results of these tests indicate that 13 out of 18 tests had lead retention values of greater than 100 percent of the feed.

Metal testing was also done at the IRF (5) with a synthetic mixture representing a Superfund type soil. The purpose of these tests was to determine the partitioning of the metals of which lead was included. All nine tests were conducted at operating conditions of about 900°C (1652°F) and about a 100 percent excess air at the incinerator outlet. These tests indicated over 100 percent recovery for lead in three of the nine tests. The average lead retention in the ash was 91.8 percent, the lowest retention 44.5 percent and the highest lead retention was 132.8 percent.

Figure 1 shows the calculated results of the lead retention at all operating conditions. At 6 percent oxygen, 50 percent excess air, and 816°C (1500°F), 151 percent of the lead was retained in the ash. At 6 percent oxygen and 982°C (1800°F), 34 percent of the lead in the feed was retained in the ash. At 11 percent excess oxygen, an average of 114 percent (Tests 1 and 5) retention of lead in the ash was attained at 816°C (1500°F), and 33 percent of the lead was retained at 982°C (1800°F).

Although mass balances of over 100 percent lead in the incinerator effluents cannot happen, the lead emissions from the system at the operating point of 816°C (1500°F) and 7 percent oxygen (50 percent excess air flow) appeared to be the best operating condition for incineration of a lead contaminated soil if it is desired to have increased lead retention in the ash and the lowest stack emissions of lead to the atmosphere.

#### CONCLUSIONS

1. The greatest amount of lead retained in the ash was (151 percent) at 816°C (1500°F) and 7.5 percent oxygen (about 50 percent excess air flow).
2. Operating conditions of the lower temperature 816°C vs. 982°C (1500°F vs. 1800°F) increased lead retention in the ash.
3. Reduced oxygen concentration (lower air flow rates) gave increased retention of the lead regardless of the operating temperature.
4. The emissions were between 6 and 8 percent of the feed (relatively flat) at 11 percent excess air regardless of temperature.

5. The emissions ranged from about 6 percent at 816°C (1500°F) to about 9 percent at 916°C (1800°F) when at 7 percent oxygen (50 percent excess air).
6. The TCLP of lead in both the feed and ash was lower than the detection limit 0.05 mg/L which was well below the 5 mg/L guidance limits.

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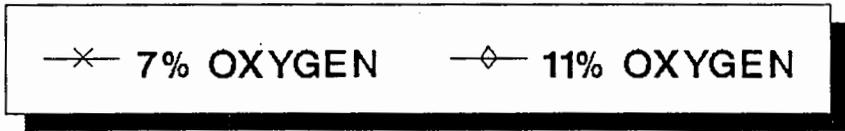
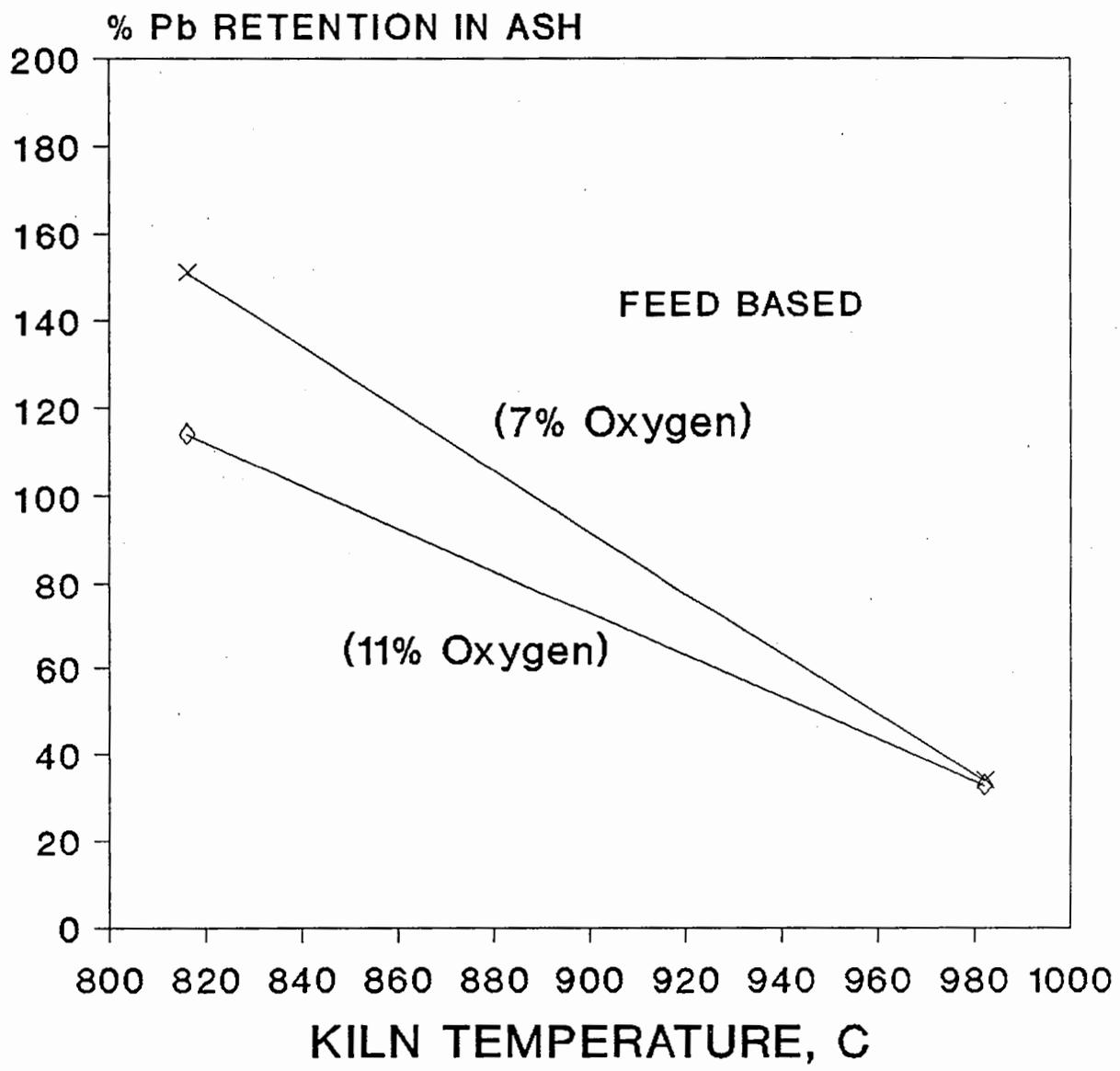
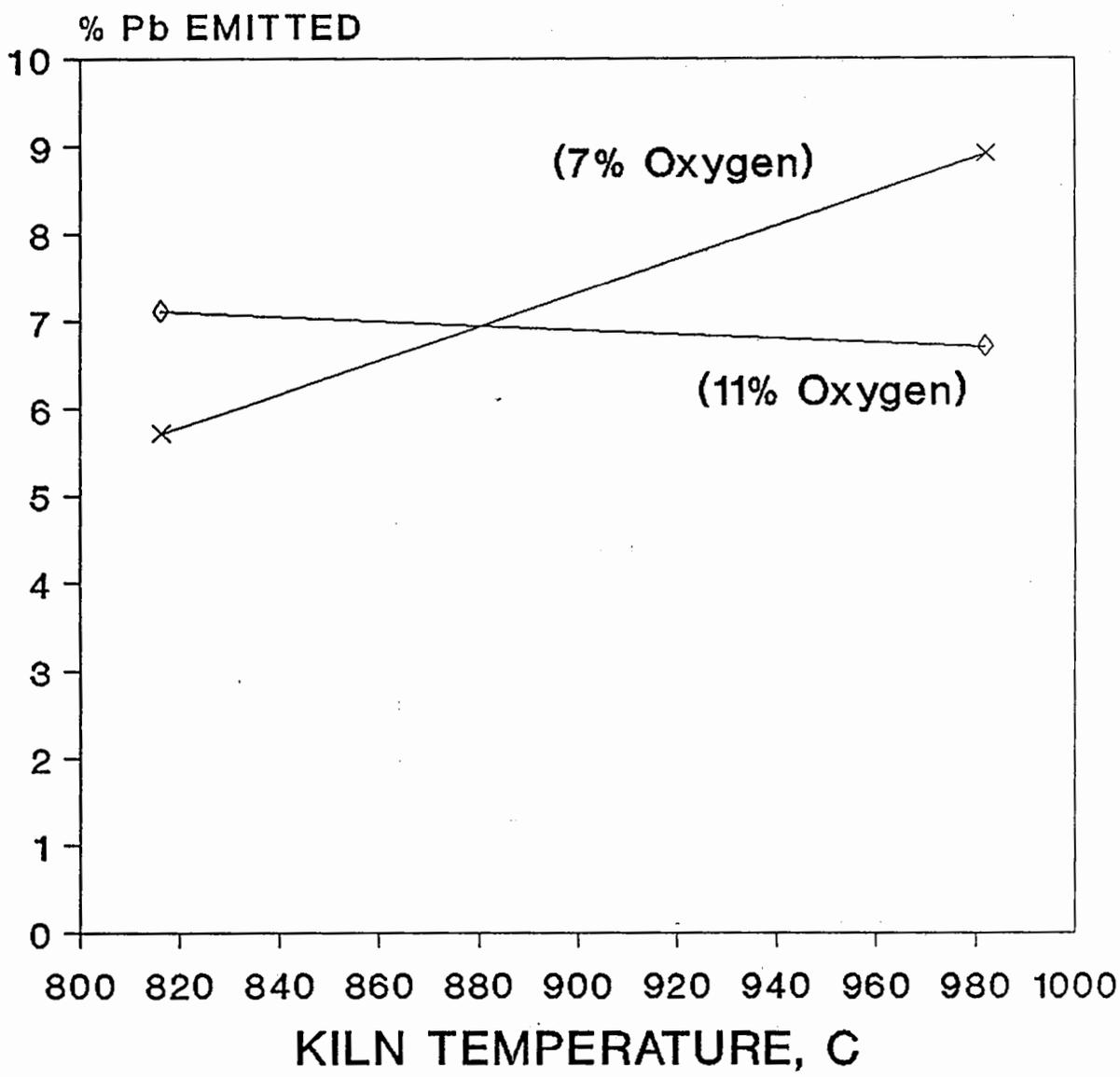
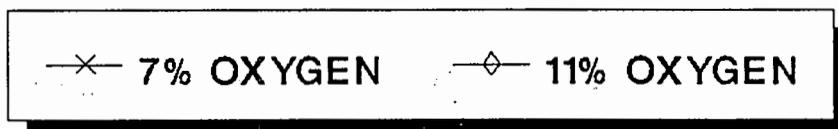
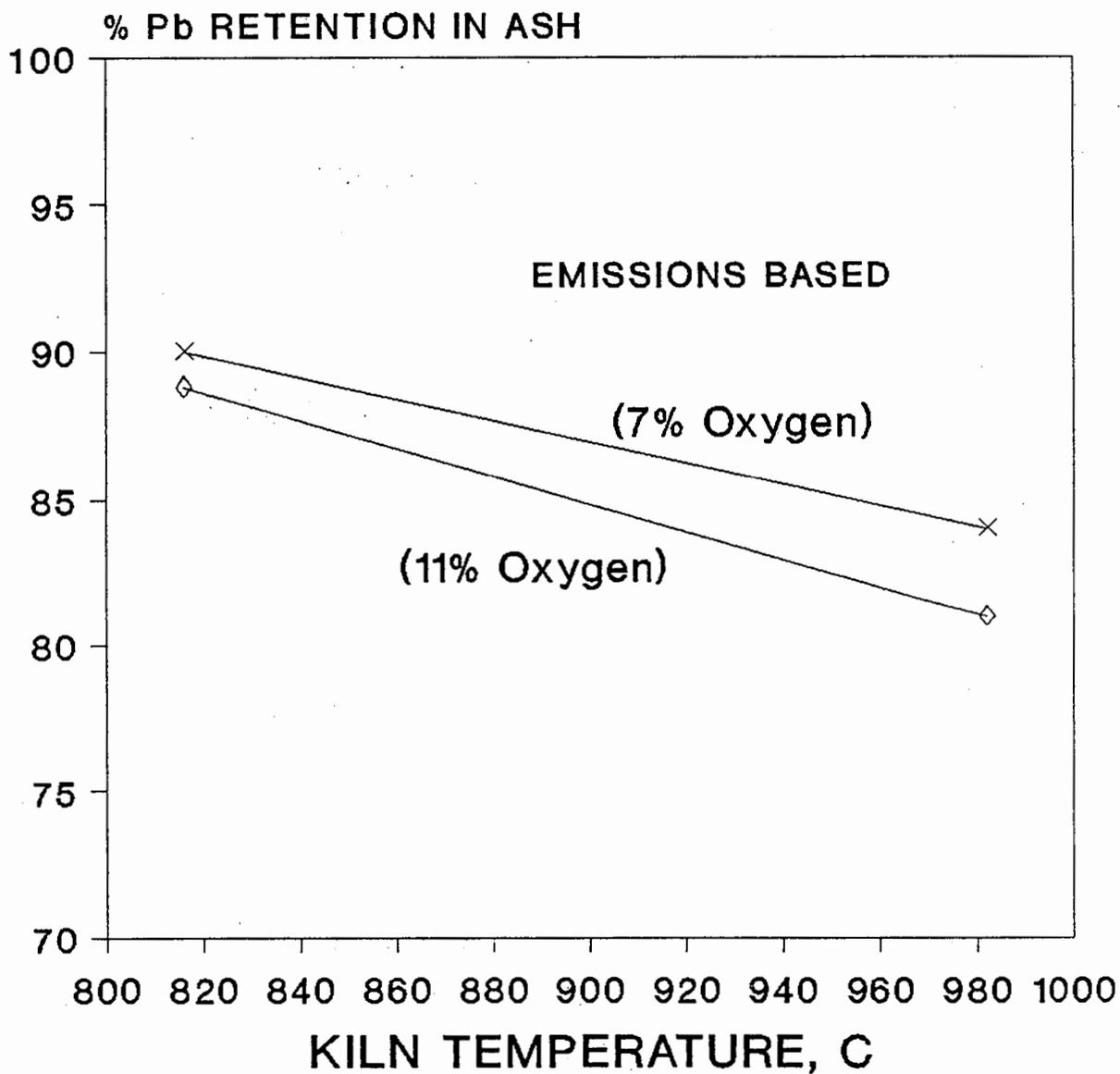


Figure 1. Lead retention in ash.



—x— 7% OXYGEN      —◇— 11% OXYGEN

Figure 2. Lead emission in stack.



**Figure 3. Lead retention in ash.**

TABLE 1. MUFFLE FURNACE TEST RESULTS

Fraction Contaminated Soil %	Fraction Background Soil %	Calculated Concentration Soil mg/kg lead (Pb)	Ash Concentration mg/kg lead (Pb)	TCLP leachate concentration mg/L
100	0	45	5.1	<0.05
80	20	39	5.1	<0.05
60	40	33	5.5	<0.05
50	50	30	4.3	<0.05
40	60	26	5.2	<0.05
20	80	20	5.8	<0.05
0	100	14	3.7	<0.05
100	(2% lime added)	44	6.9	<0.05
100	(2% alum added)	44	7.4	<0.05

Table 2. Operating Conditions and Lead Results

Test	1	2	3	4	5
Date	(9-26-89)	(9-29-89)	(9-27-89)	(9-28-89)	(10-5-89)
Kiln exit temperature, °C	832	844	994	994	839
Kiln exit temperature, °F	1529	1552	1822	1822	1541
Length test, hours	3.17	3.16	2.92	3.16	3.83
Feed rate, kg/hr	54	55	56	56	56
Scrubber water recirculating tank volume, liters*	1425	1425	1425	1425	1425
Kiln exit oxygen, percent	11.3	6.8	10.4	7.5	11.2
Scrubber blowdown, L/min	1.90	1.90	1.90	1.90	1.90
Average flue gas flow rate, acm	56	41.7	56	55.6	54.6
dsm	31.3	22.4	28.4	27.6	29.3
acfm	450	429	199	610	407
Loss on ignition, percent (moisture and organics)	17	17	17	17	17
<u>Lead concentrations</u>					
Feed (mg/kg)	21	16	27	17	20
Feed TCLP (mg/L)	<0.05	<0.05	<0.05	<0.05	<0.05
Ash (mg/kg)	31	30	11	7	26
Ash TCLP (mg/L)	<0.05	<0.05	<0.05	<0.05	<0.05
Scrubber blowdown (mg/L)	0.09	0.07	0.11	0.11	0.08
IWS exit flue gas (mg/dscm)	0.053	0.045	0.061	0.050	0.037
Total emissions, kg/hr	0.017	0.002	0.015	0.002	0.031

\*There is a precipitate in the scrubber water, quantity and identity not determined.

TABLE 3. INCINERATOR TEST RESULTS

<u>Test</u>	<u>Incinerator exit kiln temp., °C</u>	<u>% oxygen content of flue gas at kiln exit</u>	<u>Lead retention in ash, % of feed mass calculated</u>	<u>Lead retention in ash, % Calculated based on Emissions</u>	<u>Lead retention in scrubber water, % of feed mass</u>	<u>Lead in stack gas, % of feed</u>	<u>Lead balance % of feed</u>	<u>Total Emissions before Scrubber (Scrubber and Stack gas) % of feed</u>
1	816 (1500°F)	11	122	87.3	4.6	8.1	135	12.7
5	816 (1500°F)	11	106	90.3	3.5	6.2	116	9.7
2	816 (1500°F)	7	151	90	4.3	5.7	161	10.0
3	982 (1800°F)	11	33	81	2.3	6.7	42	9.0
4	982 (1800°F)	7	34	84.5	6.6	8.9	49	15.5

## FULL-SCALE POHC INCINERABILITY RANKING AND SURROGATE TESTING

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### ABSTRACT

The U.S. Environmental Protection Agency, Office of Research and Development (EPA/ORD), and the Headquarters Air Force Engineering and Services Center (HQ AFESC) are interested in evaluating the incinerability ranking of principal organic hazardous constituents (POHC's) and surrogate compounds that are used for destruction and removal efficiency (DRE) tests at hazardous waste incinerators. The results of these evaluations will aid development of a more effective and cost-efficient trial burn and performance monitoring process. As a part of the evaluation process, a test was conducted at a full-scale hazardous waste incinerator.

There were two test objectives. The first was to evaluate an incinerability ranking system commonly used by EPA. This system ranks organic compounds based on the gas-phase thermal stability under oxygen-starved conditions and is based on available experimental data. The second objective was to evaluate sulfur hexafluoride ( $SF_6$ ) as a surrogate for POHC destruction. Sulfur hexafluoride is one of the most stable compounds known with respect to thermal decomposition. Thus, it has been hypothesized that the  $SF_6$  DRE would represent a lower bound to other POHC DRE's in an incinerator. This paper presents the results of the test relative to the two test objectives.

This paper has been reviewed in accordance with the U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

The EPA/ORD and HQ AFZSC contracted to Midwest Research Institute (MRI) to evaluate the incinerability ranking of POHC's and surrogate compounds that are used for DRE tests (trial burns) at hazardous waste incinerators. The incinerability ranking evaluated is a thermal stability system developed for EPA by the University of Dayton Research Institute (UDRI). The surrogate compound evaluated is SF<sub>6</sub>. The results of these evaluations should aid development of a more effective and cost-efficient trial burn and performance monitoring process.

Incinerability of POHC's has been measured by a variety of ranking systems, the most common being based on the heat of combustion (Hc) of POHC's, with lower Hc indicating more difficult destruction. The method that has best correlated with field data is the thermal stability ranking system developed by UDRI for EPA. This system ranks POHC's based on their gas-phase thermal stability under oxygen-starved conditions. The ranking is based on a large amount of laboratory-scale experimental data. The experimental data is extrapolated through comparisons of compound structure and properties to obtain a ranking for all POHC's. Evaluation of this ranking system was one objective of this study.

The second objective of this study was to evaluate SF<sub>6</sub> DRE as a conservative indicator for the DRE of POHC's. Since promulgation of the hazardous waste incinerator performance standards in January 1981, there has been a continuing interest in a real-time surrogate compound to measure incinerator compliance with the DRE performance standard. One such possible surrogate is SF<sub>6</sub>. Sulfur hexafluoride is one of the most stable compounds known with respect to thermal decomposition. Thus, it has been hypothesized that the SF<sub>6</sub> DRE would represent a lower bound to other POHC DRE's. Furthermore, SF<sub>6</sub> can be measured at very low concentrations in stack gas on a real-time basis using onsite gas chromatographic techniques. For these reasons, using SF<sub>6</sub> injection with real-time DRE measurement represents a potentially attractive surrogate to determine compliance with DRE performance. Previous field tests conducted to gather data on SF<sub>6</sub> destruction in hazardous waste combustion devices have shown the potential of this compound as a surrogate for POHC destruction, but have not answered all concerns about its use.

The remainder of this paper presents the approach to achieving the experimental objectives, a discussion of the project results, and brief conclusions.

## APPROACH

Conducting a full-scale experimental test requires identifying and obtaining permission to test from an operating hazardous waste incinerator. Eastman-Kodak Company's chemical waste incinerator located in Rochester, New York, was identified as a suitable site, and permission was obtained to conduct the test. This incinerator was representative of many currently operating hazardous waste incinerators and was amenable to the variety of

sampling and waste spiking necessary to achieve the project objectives. Kodak personnel provided invaluable flexibility and assistance in operating the incinerator during the test.

The Kodak incineration system treats a variety of combustible liquid and solid wastes generated at the Kodak Park manufacturing site in Rochester. It consists of a rotary kiln, mixing chamber, and secondary combustion chamber, followed by a quench chamber and venturi scrubber. The thermal capacity of the kiln and secondary chamber are a nominal 90 million British thermal units per hour (Btu/h).

An overview of the design of the test matrix conducted at this incinerator is presented in Figure 1. The test was conducted over four days, with the incinerator operating at two different conditions, Condition A and Condition B. Each test condition included 12 sampling periods. Test Condition A entailed operating the incinerator at a high-temperature, low-oxygen condition while firing liquid waste to the kiln. Test Condition B involved operating the incinerator at a low-temperature, high-oxygen condition while firing only liquid and solid wastes to the kiln. The spread in temperature and oxygen concentration between the two conditions was maximized to the extent possible while remaining within acceptable combustion conditions. Temperature was the primary independent variable, while oxygen levels varied as necessary to achieve the desired temperatures.

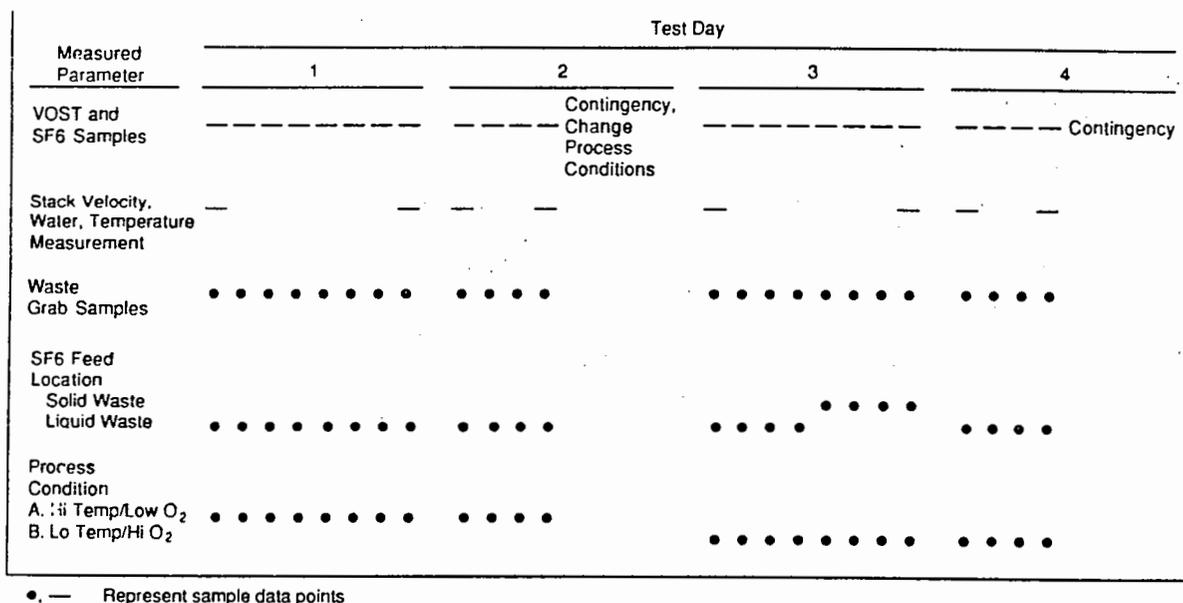


Figure 1. Overview of test matrix.

The wastes used during the test included two liquid organic waste feeds to the kiln and secondary chamber and a surrogate solid waste feed to the kiln. The physical and chemical characteristics of each stream were maintained as consistent as possible throughout the test. Liquid wastes were composed primarily of waste solvent compounds, which were blended to as homogeneous a feed as possible. Solid wastes were bulk sawdust, contained in

35-gallon (gal) fiberpaks. Some auxiliary fuel (No. 2 diesel fuel) was also used during the test.

Six volatile POHC's were spiked to or were native to the liquid waste stream, and one volatile POHC was spiked to some of the solid waste drums. The spiked liquid waste was fed via the kiln liquid waste burner. Table 1 lists the spiking compounds, their thermal stability classification, and the matrix into which they were spiked. These compounds were chosen to represent the five highest of the seven class rankings. Class 1 is the most thermally stable.

TABLE 1. TARGET POHC COMPOUNDS

Compound	UDRI class	Spiking matrix
Monochlorobenzene	1	Liquid waste
Methylene chloride	2	Liquid waste
Tetrachloroethylene	2	Liquid waste
Methyl ethyl ketone	3	Liquid waste
Chloropropene	4	Liquid waste
1,1,1-Trichloroethane	5	Liquid waste
Toluene	2	Solid waste

The SF<sub>6</sub> was spiked into both the liquid and solid wastes during different portions of the test. During days 1, 2, and 4, SF<sub>6</sub> was spiked into the liquid waste fed to the kiln. During day 3, SF<sub>6</sub> was spiked alternately into the solid and liquid waste streams as defined in Figure 1. The SF<sub>6</sub> spiked to the solid waste was microencapsulated, the capsules packaged into 250-milliliter (ml) plastic bottles, and the bottles placed into drums of waste fed to the incinerator. These same drums were the ones spiked with toluene. The SF<sub>6</sub> spiked to the liquid waste was injected as a gas into the liquid waste feed line. The injection point was located upstream of the kiln burner nozzle.

Measurements of the emissions of POHC's and SF<sub>6</sub> were made in a transition duct located between the secondary combustion chamber and the quench. A volatile organic sampling train (VOST), as described in SW-846 Method 0030, was used to collect samples of the POHC's. These samples were analyzed by gas chromatography/mass spectrometry (GC/MS) using selected ion monitoring (SIM). The SIM analysis provided a very low detection limit that allowed quantification of very high DRE's. The SF<sub>6</sub> samples were collected in tedlar bags and analyzed onsite with a gas chromatograph equipped with an electron capture detector. Composite samples of the waste feeds were collected for analysis of POHC's by GC/MS.

## RESULTS

This section presents a brief discussion of the process operation followed by the project results. The results are organized by the two project objectives described earlier.

## PROCESS OPERATION

Process operation was replicated closely from day to day during the test except for the planned variations in waste feed rates and combustion temperature. Table 2 shows the average values for the key process variables for each of the two test conditions. The waste feed rates were changed to achieve the desired combustion temperature change of about 200°F between test conditions.

TABLE 2. KEY PROCESS OPERATING DATA

Parameter	Units	Condition A	Condition B
<b>Kiln</b>			
Liquid waste feed rate	lb/h	1,760	1,240
Solid waste feed rate	lb/h	0	830
Temperature	°F	1730	1510
Combustion air flow	acfm	7,200	7,220
<b>SCC</b>			
Liquid waste feed rate	lb/h	2,350	2,130
Temperature	°F	1920	1,700
Combustion airflow	acfm	4,330	3,180
<b>SCC exit</b>			
Oxygen	%	15.1	15.7
Carbon monoxide	ppm	4	1

The concentration of each individual POHC in the waste feeds was kept relatively constant throughout the test. The concentration varied between POHC's from 2 to 25 percent, depending on the amount that was native to the waste. Sulfur hexafluoride was fed at a rate of 2 to 10 pounds per hour (lb/h) in the liquid waste feed line and 0.15 lb/h in the solid waste.

## POHC INCINERABILITY RANKING

This section presents the data on POHC DRE's gathered during this study and an evaluation of the ranking of these DRE's compared to the ranking predicted by EPA's thermal stability ranking system. One of the seven POHC's selected for the study (methyl ethyl ketone) was present in the waste feeds at unexpectedly low concentrations; therefore, the following discussion addresses only the other six POHC's.

Table 3 shows the average DRE's for each of the two process operating conditions. These two conditions differed principally in that Condition A had combustion temperatures about 200°F higher than Condition B. The DRE data show little difference between these two conditions, with the possible exception of methylene chloride. Methylene chloride DRE's appeared to be slightly higher for Condition A. In general, daily averages differed as much as the condition averages, and the differences were within expected sampling and analysis accuracy. Because these differences between the conditions were

small and appeared random, data for both conditions were combined for the evaluation of the ranking discussed below.

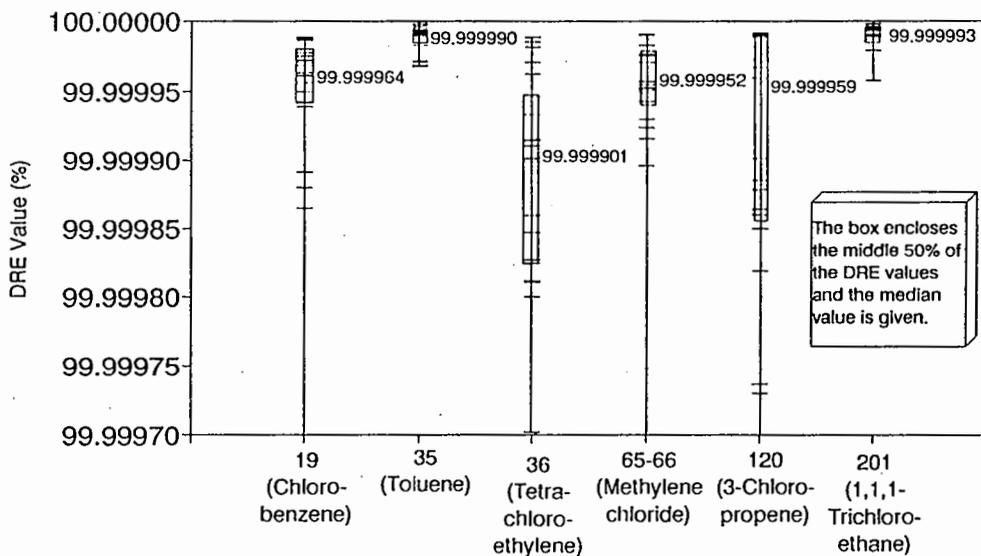
TABLE 3. AVERAGE POHC DRE's

POHC	Average DRE, percent	
	Test Condition A	Test Condition B
Chlorobenzene	99.999955	99.999923
3-Chloropropene	99.99984	99.999904
Methylene chloride	99.999969	99.99990
Tetrachloroethene	99.99988	99.99986
Toluene	99.999985	99.999991
1,1,1-Trichloroethane	99.999991	99.999991

Figure 2 displays the DRE results compared to the predicted thermal stability ranking. The measured DRE's are shown on the figure as the range of individual sample values, the middle 50 percent of the values (boxes on the figure), and the median values for each POHC. The data are arrayed on the figure by POHC with data for the hardest-to-destroy POHC to the left, increasing to easier-to-destroy POHC's to the right. The thermal stability/incinerability index is shown at the bottom of the figure. If the ranking of the measured DRE's matched the ranking predicted by the thermal stability index, the DRE's should increase from POHC to POHC from left to right on the figure.

Considering only the median value for each POHC, four of the six POHC's ranked correctly relative to one another. The two that did not rank as predicted, chlorobenzene and toluene, were easier to destroy than predicted. Considerable overlap occurs, however, in the ranges of values for each POHC. This data scatter is greater than typically observed for VOST trial burn results for two reasons. First, each data point is the analytical result for a single pair of traps, while trial burn results are expressed as an average of several pairs of traps. This averaging reduces the apparent scatter in the data. Second, the results of the SIM analysis had more scatter than typical VOST analysis results because of the extremely low levels that were quantified.

The measured DRE values were subjected to nonparametric (rank order) statistical tests for further evaluation. The statistical tests showed a high degree of consistency in the measured ranking from sample to sample throughout the test. They also confirmed the discussion above relative to the agreement with the predicted ranking.



Thermal Stability Incinerability Index

Figure 2. DRE for each POHC.

Two factors that related to how the data were reduced were investigated to determine if they affected the observed ranking of the POHC's. These factors were blank correction of the data and the relationship between POHC concentration in the waste and DRE. Blank corrections are discussed first below.

Because of the low levels of detection achieved with the SIM analysis, blank trap levels were a problem for some compounds, most noticeably for toluene, 3-chloropropene, and 1,1,1-trichloroethane. When blank levels are significant, they bias the concentration and emission rates high and the DRE's low. To check the effect on ranking of the calculated DRE's, a simple subtraction of blank levels was used to correct the data. Figure 3 shows the unadjusted and blank-corrected DRE's. Blank correction increased all the DRE's, but the ranking trend did not change.

Figure 3 also shows the feedrate-normalized DRE's. An earlier study identified the effect of POHC concentration in the waste feed on measured DRE's. Destruction and removal efficiency increases as the POHC concentration increases. A similar relationship was found using the data from this study, which was used to calculate the feedrate-normalized DRE's plotted in Figure 3. This correction of the calculated DRE's increased some values, decreased others, and did not change others. However, as happened for the blank-corrected DRE's, the ranking trend did not change.

Figure 3 also shows DRE's calculated considering both of the above corrections together. Again, the ranking trend is the same. The effect of these corrections, however, was to decrease the differences in DRE from POHC to POHC. The lowest and highest corrected DRE's differed by a factor of only 20.

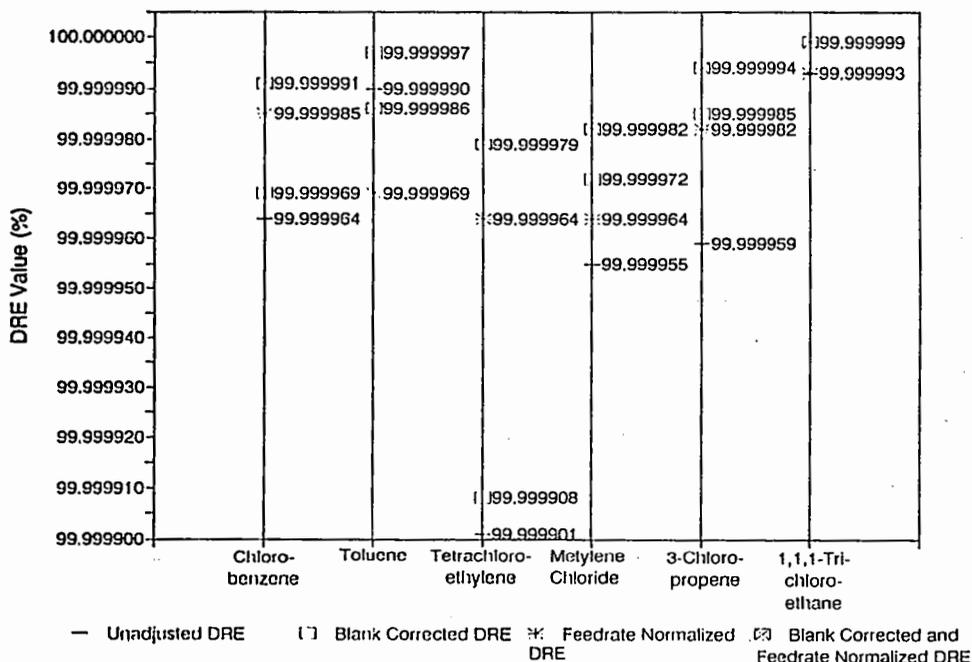


Figure 3. Comparison of corrected DRE values.

## SF<sub>6</sub> DESTRUCTION

The study objective related to SF<sub>6</sub> focused on two questions about the use of this compound as a surrogate compound to measure POHC DRE. The first question concerned the effect on SF<sub>6</sub> DRE of the method of introducing the SF<sub>6</sub> to the incinerator. Conceivably, the method of introduction could affect what combustion conditions the SF<sub>6</sub> experiences. Historically, studies of SF<sub>6</sub> as a surrogate compound have introduced the SF<sub>6</sub> by spiking it into the liquid waste line or combining it with the combustion air. No study was identified where SF<sub>6</sub> was introduced with solid waste.

During one day of the test, SF<sub>6</sub> was spiked alternately into the solid and liquid waste streams. For the first half of the day, SF<sub>6</sub> was spiked as a gas into the liquid waste feed line. During the second half of the day, the microencapsulated SF<sub>6</sub> was placed into the drums of solid waste to be fed to the incinerator. No other process parameters were changed on this day. The average DRE's measured when the SF<sub>6</sub> was fed with the liquid and solid wastes were 99.989 and 99.986 percent, respectively. Thus, the method of feeding SF<sub>6</sub> into the incinerator via liquid or solid waste to the kiln did not affect the DRE.

The second question was whether SF<sub>6</sub> gives a conservative value of DRE relative to the POHC DRE's. Earlier studies have generally shown that SF<sub>6</sub> DRE is conservative (has a lower DRE) relative to POHC DRE's. Figures 4 and 5 show that the data from this study confirm the earlier studies. Figure 4 shows that the SF<sub>6</sub> DRE during Condition A (the higher-combustion-temperature condition, where the highest SF<sub>6</sub> DRE's were measured) was an order of

magnitude or more lower than the POHC DRE's. Figure 5 shows the same result during Condition B, but the SF<sub>6</sub> DRE's were even more conservative.

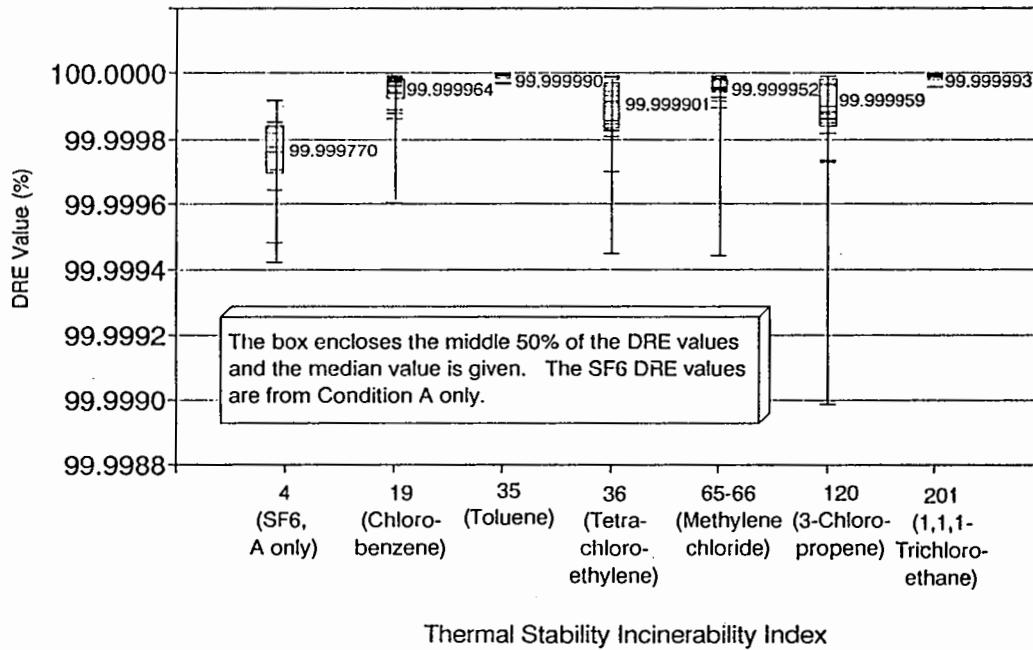


Figure 4. SF<sub>6</sub> and POHC DRE values.

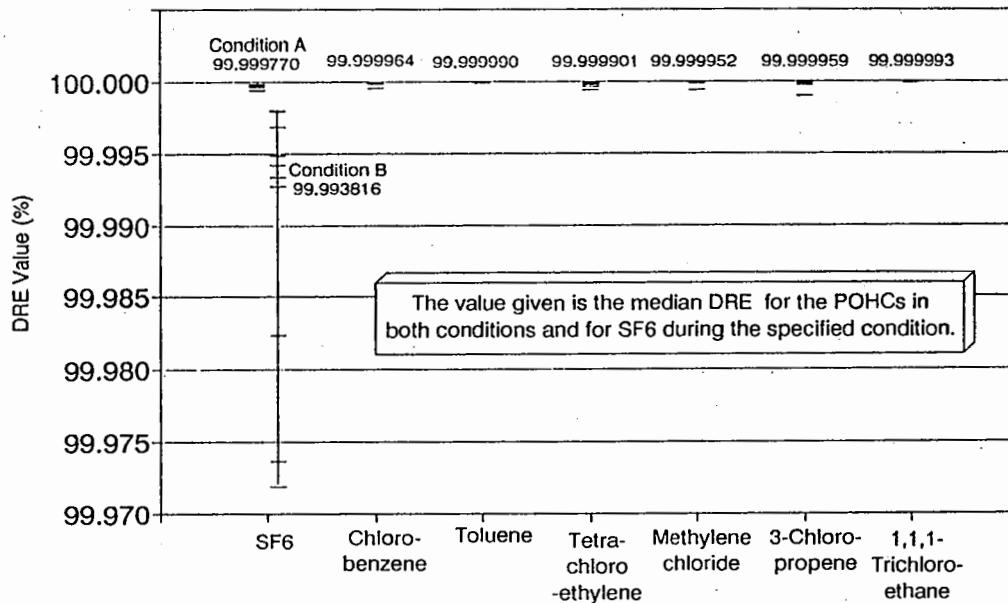


Figure 5. SF<sub>6</sub> and POHC DRE values.

As can be seen on Figure 5, the SF<sub>6</sub> DRE's measured during Condition B were considerably lower than the SF<sub>6</sub> DRE's measured during Condition A. These data indicate a dependence of SF<sub>6</sub> DRE on combustion temperature. Combustion temperatures during Condition A were 1730°F and 1920°F in the kiln and secondary chamber, respectively. During Condition B, they were 1510°F and 1700°F, respectively. Thus, the SF<sub>6</sub> DRE decreased from 99.9998 to 99.994 percent, with a 200°F drop in combustion temperature. Earlier discussions showed that a similar dependence on combustion temperature was not observed for the POHC's. As a result, SF<sub>6</sub> becomes a more conservative indicator as combustion temperature decreases.

## CONCLUSIONS

Below are brief statements of the primary conclusions from this study.

1. The DRE for POHC's ranked highest by the thermal stability ranking system (those easiest to destroy) generally followed the ranking order predicted by the system.
2. The DRE's for the two POHC's studied that were ranked lowest by the system (chlorobenzene and toluene) did not agree with the predicted ranking order. They were easier to destroy than predicted.
3. The 200°F change in combustion temperature between test conditions did not affect the POHC DRE's or the observed ranking order.
4. The measured ranking order was very consistent from test period to test period (sample to sample).
5. The DRE measured for SF<sub>6</sub> was lower than the DRE's for all the POHC's studied in this project; thus, SF<sub>6</sub> was a conservative indicator of POHC DRE.
6. The DRE for SF<sub>6</sub> had a distinct dependence on combustion temperature. A decrease in temperature of about 200°F caused a decrease in SF<sub>6</sub> DRE of about one order of magnitude.
7. The method of feeding SF<sub>6</sub> to the incinerator (in the liquid waste versus solid waste feed to the kiln) did not affect the DRE.

EPA's MOBILE VOLUME REDUCTION UNIT FOR SOIL WASHING

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ABSTRACT

This paper discusses the design and initial operation of the U.S. Environmental Protection Agency's (EPA) Mobile Volume Reduction Unit (VRU) for soil washing. Soil washing removes contaminants from soils by dissolving or suspending them in the wash solutions (which can be later treated by conventional wastewater treatment methods) or by volume reduction through simple particle size separation techniques. Contaminants are primarily concentrated in the fine-grained (<0.063 mm, 0.0025") soil fraction. The VRU is a pilot-scale mobile system for washing soil contaminated with a wide variety of heavy metal and organic contaminants. The unit includes state-of-the-art washing equipment for field applications.

The VRU equipment was originally conceived by the EPA. It was designed and fabricated by Foster Wheeler Enviresponse, Inc. under contract to EPA's Risk Reduction Engineering Laboratory (RREL) in Edison, New Jersey, with the following objectives:

1. To make available to members of the research community and to the commercial sector the results of government research on a flexible,

multi-step, mobile, pilot-scale soil washer capable of running treatability studies on a wide variety of soils;

2. To demonstrate the capabilities of soil washing; and
3. To provide data that facilitate scaleup to commercial size equipment.

The design capacity of the VRU is 100 lb/hr of soil, dry-basis. The VRU consists of process washing equipment and utility support services mounted on two heavy-duty semi-trailers. The process trailer equipment accomplishes material handling, organic vapor recovery, soil washing, coarse soil screening, fine particle separation, flocculation/clarification, and steam generation via a boiler. The utility trailer carries a power generator, a process water cleanup system, and an air compressor. The VRU is controlled and monitored by conventional industrial process instrumentation and hardware.

Shakedown operations are currently in progress and future plans include testing EPA-produced synthetic soil matrix (SSM) spiked with specific chemical pollutants. The addition of novel, physical/chemical treatment processes, such as sonic/ultrasonic cleaning and acid leaching, will expand the VRU's extraction capability in soil decontamination.

## INTRODUCTION

Section 121(b) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) mandates the EPA to select remedies that "utilize permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable" and to prefer remedial actions in which treatment "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants, and contaminants as a principal element."

In most cases soil washing technologies are used in conjunction with other remedial methods for the separation/segregation and volume reduction of hazardous materials in soils, sludges, and sediments. In some cases, however, the process can deliver the performance needed to reduce contaminant concentrations to acceptable levels and, thus, serve as a stand-alone technology. In treatment combinations, soil washing can be a cost-effective step in reducing the quantity of contaminated material to be processed by another technology, such as thermal, biological, or physical/chemical treatment. In general, soil washing is more effective on coarse sand and gravel; it is less successful in cleaning silts and clays.

A wide variety of chemical contaminants can be removed and/or concentrated through soil washing applications. Removal efficiencies depend on both the soil characteristics (e.g., soil geology and particle size) and the processing steps contained within the soil washer. Experience has shown that volatile organics can be removed with 90+% efficiency. Semivolatile organics are removed to a lesser extent (40-90 percent). They usually require the addition of surfactants to the wash water. Surfactants are surface-active or wetting agents, that reduce the surface tension at the interface between the hydrophobic contaminants and the soil, thereby promoting release of the contaminants into the aqueous extraction medium.

Metals which are less soluble in water, often require acids or chelating agents for successful soil washing. A chelating agent, such as ethylenediaminetetraacetic acid (EDTA), bonds with the metal and facilitates

solubilization in the extraction medium.

The VRU process can be applied to the treatment of soils contaminated with hazardous wastes such as wood-preserving chemicals (pentachlorophenol, creosote), electroplating residues (cyanides, heavy metals), organic chemical production residues, and petroleum/oil residues. The applicability of soil washing to general contaminant groups and soil types is shown in Table 1. This table has been reproduced from an EPA report, "Treatment Technology Bulletin - Soil Washing," dated May 1990.

The EPA has developed the VRU to meet the following objectives:

1. To make available to members of the research community and to the commercial sector the results of government research on a flexible, multi-step, mobile, pilot-scale soil washer capable of running treatability studies on a wide variety of soils;
2. To demonstrate the capabilities of soil washing; and
3. To provide data that facilitates scaleup to commercial size equipment.

The EPA plans to investigate other extraction processes which may be added to the VRU at a later date. The addition to the VRU of novel physical/chemical treatment processes, such as sonic/ultrasonic cleaning and acid leaching, will expand its overall extraction capability in soil decontamination.

#### SYSTEM DESCRIPTION

The VRU is a mobile, pilot-scale washing system for stand-alone field use in cleaning soil contaminated with hazardous substances. The VRU is designed to decontaminate certain soil fractions using state-of-the-art washing equipment. The total system consists of process equipment and support utility systems mounted on two heavy-duty, semi-trailers.

TABLE 1. APPLICABILITY OF SOIL WASHING TO GENERAL CONTAMINANT GROUPS FOR VARIOUS SOILS

<b>Contaminant Groups</b>		<b>Matrix</b>	
		<b>Sandy/ Gravelly Soils</b>	<b>Silty/Clay Soils</b>
<b>Organic</b>	Halogenated volatiles	■	▼
	Halogenated semivolatiles	▼	▼
	Nonhalogenated volatiles	■	▼
	Nonhalogenated semivolatiles	▼	▼
	PCBs	▼	▼
	Pesticides (halogenated)	▼	▼
	Dioxins/Furans	▼	▼
	Organic cyanides	▼	▼
	Organic corrosives	▼	▼
<b>Inorganic</b>	Volatile metals	■	▼
	Nonvolatile metals	■	▼
	Asbestos	□	□
	Radioactive materials	▼	▼
	Inorganic corrosives	▼	▼
	Inorganic cyanides	▼	▼
<b>Reactive</b>	Oxidizers	▼	▼
	Reducers	▼	▼
<p>■ Good to Excellent Applicability: High probability that technology will be successful</p> <p>▼ Moderate to Marginal Applicability: Exercise care in choosing technology</p> <p>□ Not Applicable: Expert opinion that technology will not work</p>			

Figure 1, General Block Diagram, shows the VRU basic pilot plant subsystems as follows:

1. Soil handling and conveying
2. Organic vapor recovery
3. Soil washing and coarse screening
4. Fines/floatables gravity separation
5. Fines flocculation/water clarification and solids disposal
6. Water treatment
7. Utilities - electric generator, steam boiler, and compressed air unit

The generator, air compressor, water heater, water filters/carbon adsorbers, recycle water pump, gasoline tank (for the generator) and delisting tank are located on the utility trailer. All remaining equipment is located on the process trailer. The VRU system is controlled and monitored by conventional industrial process instrumentation and hardware, including safety interlocks, alarms, and shutdown features.

## PROCESS DESCRIPTION

Figures 2, 3, and 4 present the Process Flow Diagram for all VRU subsystems in terms of their process equipment functions.

### 1. Soil Handling and Conveying

Raw soil is delivered from battery limits to a vibrating grizzly that separates the particles greater than  $+\frac{1}{2}$ " into a drum for redeposit and collects the smaller particles ( $-\frac{1}{2}$ " +0) for transfer to the feed surge bin. (One half-inch is the maximum particle size that can be handled in the mini-washer, but smaller screen sizes may be selected.) From this bin, the  $-\frac{1}{2}$ " soil is conveyed through a steam-jacketed screw conveyor where the volatile organics and water are vaporized. Both live steam and jacketed steam can be introduced so that the efficiency of the steam extraction can be determined. The conveyor flow is adjusted by a speed

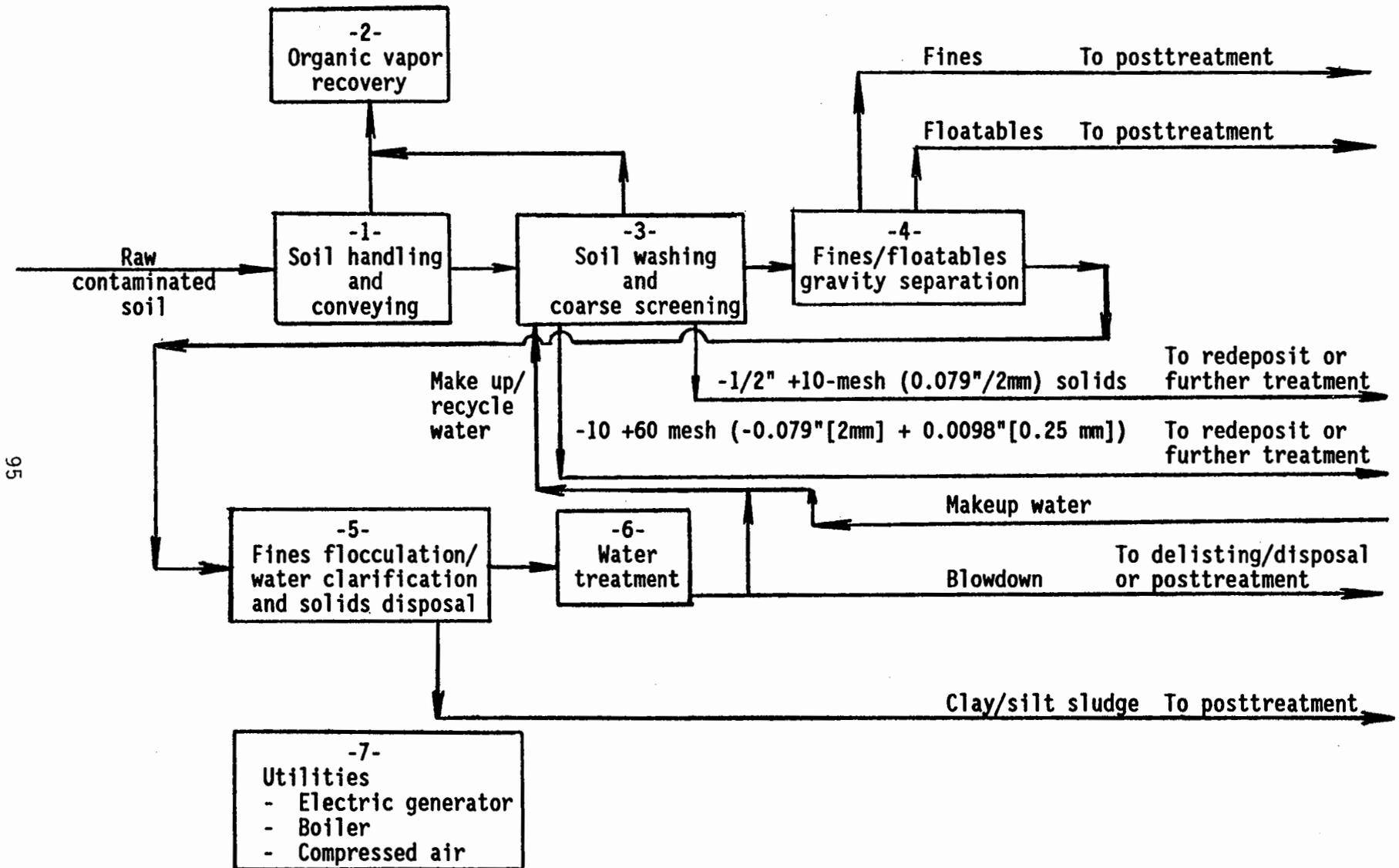


Figure 1. General Block Diagram - The U.S. Environmental Protection Agency Volume Reduction Unit (VRU) for Soil Washing

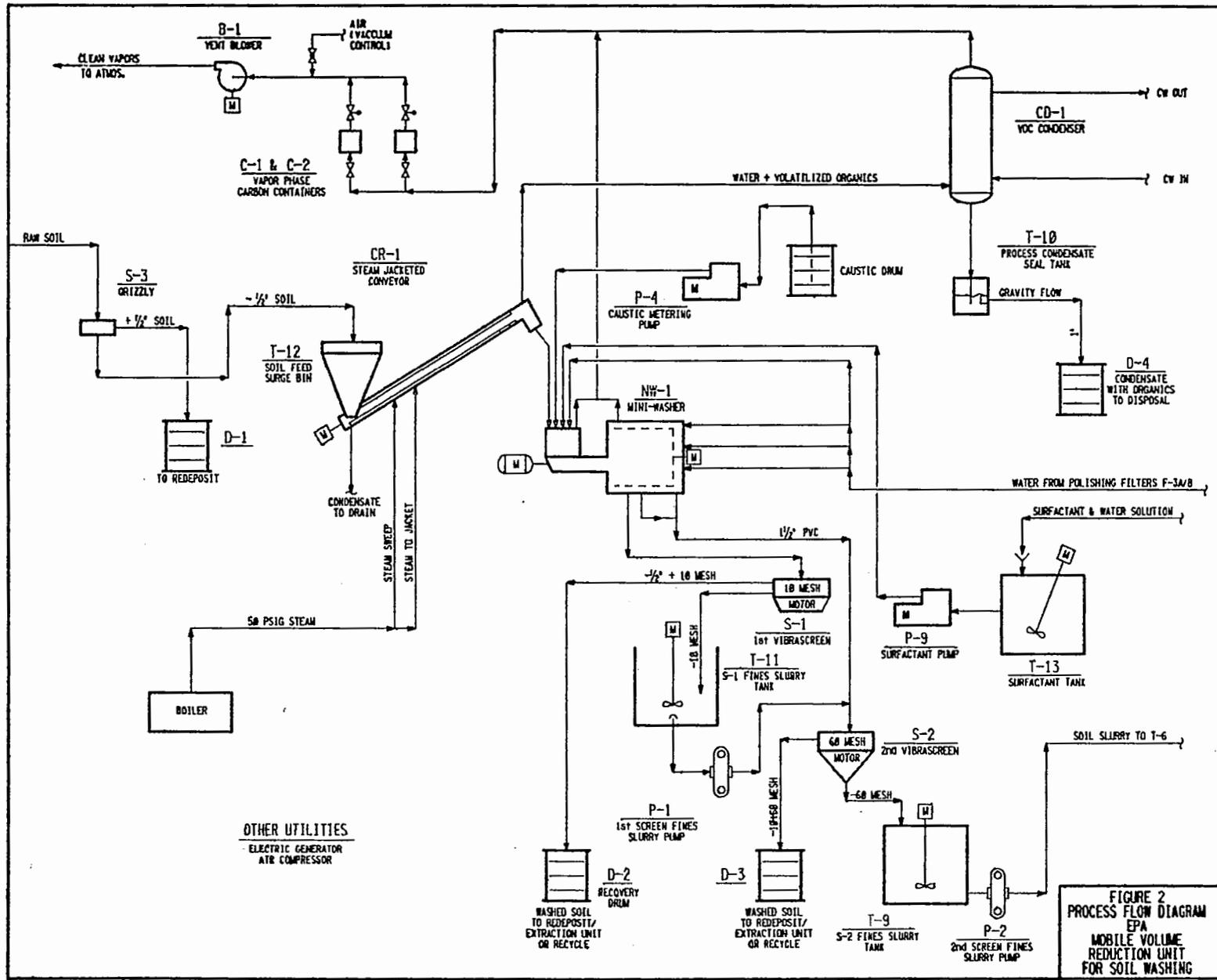


FIGURE 2  
PROCESS FLOW DIAGRAM  
EPA  
MOBILE VOLUME  
REDUCTION UNIT  
FOR SOIL WASHING

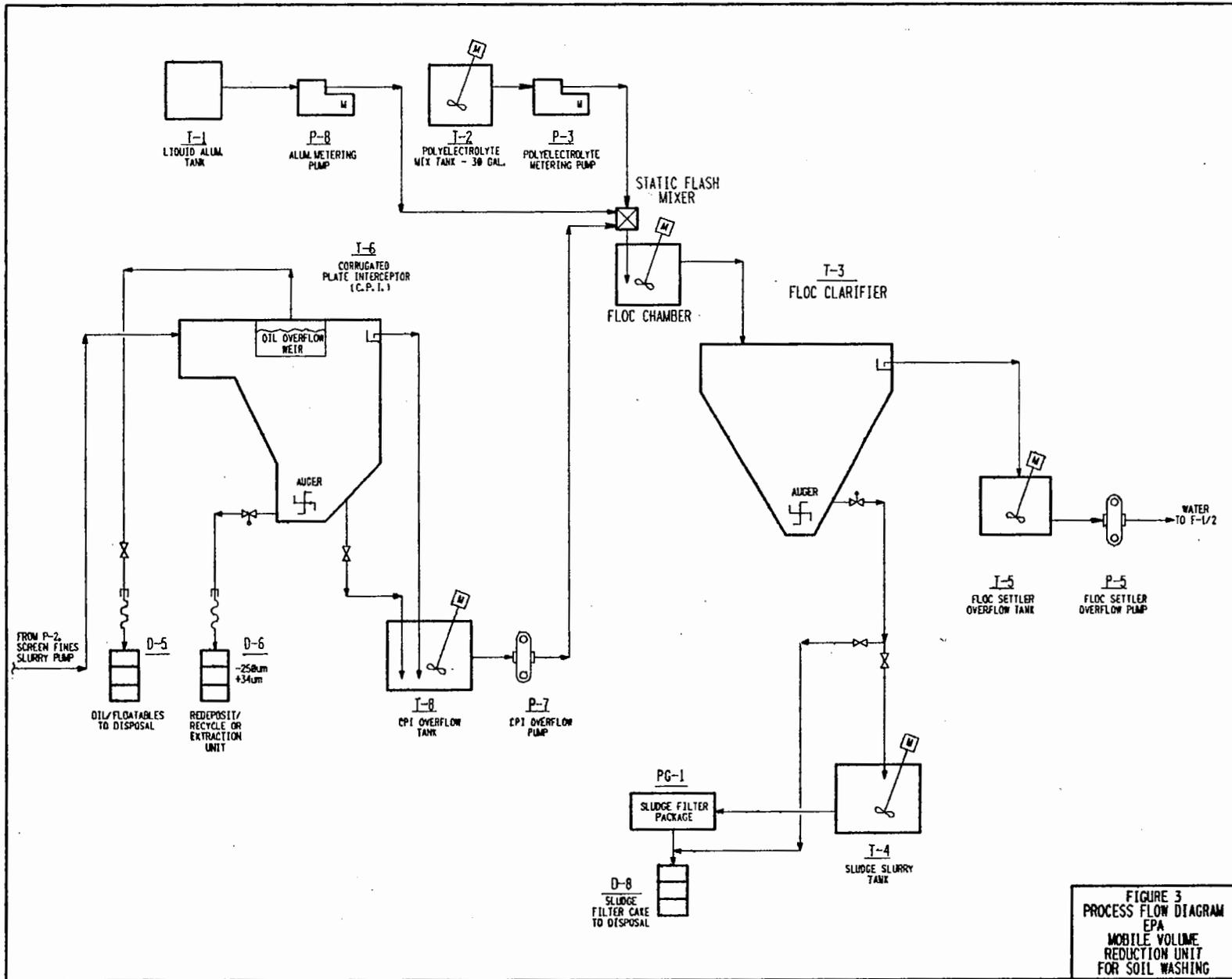


FIGURE 3  
PROCESS FLOW DIAGRAM  
EPA  
MOBILE VOLUME  
REDUCTION UNIT  
FOR SOIL WASHING

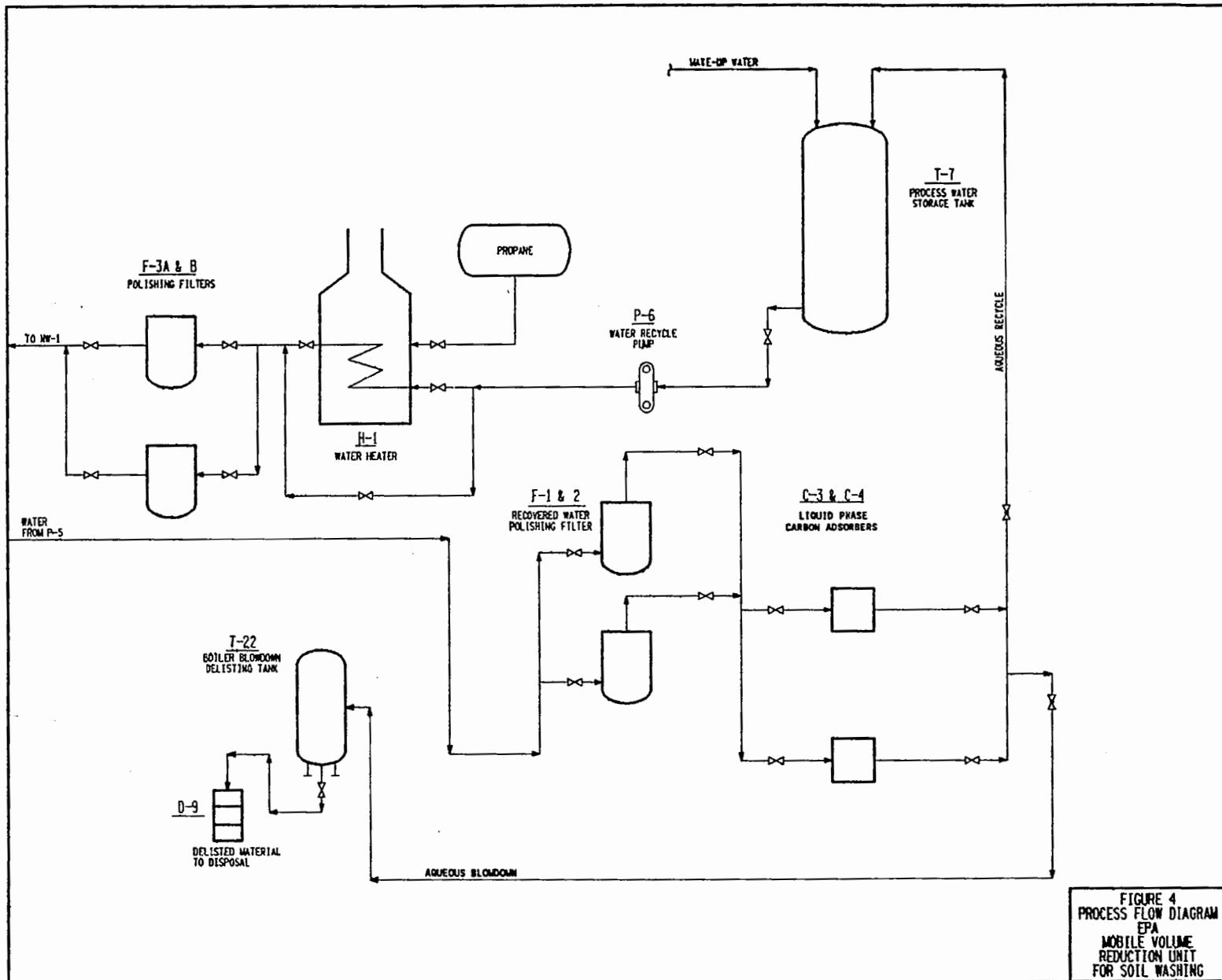


FIGURE 4  
 PROCESS FLOW DIAGRAM  
 EPA  
 MOBILE VOLUME  
 REDUCTION UNIT  
 FOR SOIL WASHING

controller on the conveyor motor. The solids pass through a motor-operated rotary valve (which prevents air infiltration), then into the feed hopper of the mini-washer.

## 2. Organic Vapors Recovery

Volatiles stripped from the soil in the screw conveyor are either collected in the volatile organic compounds (VOC) condenser and fall by gravity into the process condensate seal tank, or are adsorbed in vapor-phase activated carbon containers located upstream of the vent blower.

The spent carbon will be periodically replaced based on vent gas analyses. The vapor train is maintained under vacuum by an induced draft blower. The vacuum level is adjusted by manual admittance of atmospheric air upstream of the blower to maintain a slight negative pressure on the vapor system. Clean vapors, leaving the blower, vent to the atmosphere.

## 3. Soil Washing and Coarse Screening

Soil is fed to the mini-washer at a controlled rate of approximately 100 lb/hr by the screw feeder. Filtered wash water, which can be heated to 150°F (maximum), is added to soil in the feed hopper and also sprayed onto an internal slotted trommel screen (with a 10-mesh (0.079") slot opening) mini-washer. Five manually controlled meters can control the flow up to approximately 10:1 overall weight ratio water to soil. Hot water should be more efficient in extracting contaminants, but heating is optional. When required, dilute surfactant/detergent, and/or caustic can be metered at a controlled rate into the feed hopper.

Two vibrating screens, equipped with anti-blinding devices, are provided to continuously segregate soil into various size fractions. These screened fractions can be collected to measure the effectiveness of contaminant removal for each soil fraction recovered, and to determine the

effectiveness of soil washing in cleaning a particular contaminated soil fraction to achieve sufficient volume reduction.

Mini-washer overflow, containing the coarser solids, falls onto the first 10-mesh (0.079"/2 mm) vibrascreen. First vibrascreen overflow (-½" + 10 mesh (0.079"/2 mm)) solids flow by gravity down to a recovery drum. The underflow is pumped at a controlled rate, using a progressing cavity pump, onto the second 60-mesh (0.0098"/0.25 mm) vibrascreen where it is joined by the Mini-Washer underflow.

The overflow from the second vibrascreen (- 10-mesh (0.079") + 60-mesh (0.0098")), is gravity fed to another recovery drum. Second vibrascreen underflow (a fines slurry) drains into an agitated tank. The VRU is designed with the following flexibility:

- a. The mesh sizes for both the mini-washer and vibrascreens can be varied (i.e., the screen size could be 20- or 30-mesh (0.033" or 0.023")).
- b. Additional soil cleaning by use of water sprays or steam sprays will be evaluated for each vibrascreen.
- c. Screened soil fractions, collected in the recovery drums, can be redeposited if sufficiently cleaned or further cleaned by addition of rinse water, followed by reslurrying and pumping the slurry back over the screens (recycle mode). In the future these soil fractions will be sent for treatment by various extraction units currently under development by EPA's RREL in Edison, New Jersey.

#### 4. Fines/Floatables Gravity Separation

Slurry from the second screen (fines slurry) tank, containing particles less than 60-mesh (0.0098"/0.25 mm) in size, is pumped to a Corrugated Plate Interceptor (CPI). Material lighter than water (floatables such as oil) will overflow an internal weir, collect in a compartment within

the CPI, and drain by gravity to a drum for disposal. CPI-settled solids (soil particles - 60- to about 400-mesh (0.0098" to about 0.0015") will be discharged by the bottom auger to a recovery drum. The VRU has the flexibility to redeposit or further clean these settled soils, if required, by addition of rinse water followed by pumping the slurry back through the CPI. As mentioned above, these soils could also be sent, in the future, to an extraction unit.

#### 5. Fines Flocculation, Water Clarification, and Solids Disposal

Aqueous slurry, containing fines less than about 400-mesh (34 um/ 0.0014"), overflow the CPI and gravity feed into an agitated tank. The slurry is then pumped to a static flash mixer located upstream of the floc clarifier's mix tank. Flocculating chemicals are introduced into this static flash mixer. Typically, liquid alum and aqueous polyelectrolyte solutions are metered into the static flash mixer to neutralize the repulsive electrostatic charges on colloidal particles (clay/humus) and promote coagulation. The fines slurry is discharged into the floc chamber which has a varispeed agitator for controlled floc growth (sweep flocculation). Sweep flocculation refers to the adsorption of fine particles onto the floc (colloid capture) and continuing floc growth to promote rapid settling of the floc and its removal from the aqueous phase. The floc slurry overflows into the clarifier (another corrugated plate unit). Bottom solids are gravity fed by an auger to a drum for disposal, or to the sludge slurry tank (depending on solids concentration) for subsequent concentration in a filter package unit. Concentrated cake from the filter is discharged to another drum for disposal. This system has the ability to clarify the process water and dewater the sludge. The efficiency of solids dewatering can be determined, and cost savings estimated, for trucking waste sludge to a disposal/treatment site.

#### 6. Water Treatment

Clarified water is polished with the objective of reducing suspended

solids and organics to low levels that permit recycle of spent wash-water. Water is pumped from the floc settler overflow tank at a controlled rate through cartridge-type polishing filters operating in parallel, in order to remove soil fines greater than 10-um ( $3.94 \times 10^{-4}$ "). One um ( $3.9 \times 10^{-5}$ ") cartridges are available, if required.

Water leaving the cartridge filter flows through activated carbon drums for removal of hydrocarbons. The carbon drums may be operated either in series or parallel, and hydrocarbon breakthrough monitored by sampling. A drum will be replaced when breakthrough has been detected.

In order to recycle water and maintain suitable dissolved solids and organic levels, aqueous bleed (blowdown) to the boiler delisting tank may be initiated at a controlled rate. Delisted material will be sealed in drums and sent for disposal in accordance with respective state and local regulations.

Treated recycle (recovered) water is sampled for analysis before it flows into the process water storage tank. Supplementary water is fed into this tank from a tank truck. Recovered and added water is pumped by the water recycle pump (and optionally fed to the water heater) for subsequent feed to the mini-washer. A side stream from the water recycle pump is utilized as cooling water in the VOC condenser and either returned to the process water storage tank or sent to the sewerage system.

## 7. Utilities Systems

The VRU is equipped with a steam boiler, electric generator, and a compressed air system.

## Field Operations

While in the field, the VRU would be supported by a decontamination trailer, a mobile treatability lab/office, and a storage trailer for supplies,

spare parts, miscellaneous tools, etc.

### Summary of VRU Features

1. The VRU is a mobile, pilot-scale washing system for field use in cleaning soil contaminated with hazardous materials, using state-of-the-art washing equipment and support utilities.
2. The unit has the ability to remove VOCs by steam heating and stripping.
3. It is capable of washing with water (in combination with surfactants/detergents) up to a 10:1 water to soil ratio while also varying water temperature from ambient to 150°F.
4. The mini-washer screen and vibrascreens can be varied in mesh size. Additional use of soil cleaning by water or steam sprays on the vibrascreen decks can be evaluated.
5. Three screened soil fractions (including CPI-settled solids) can be further cleaned by slurring with the addition of rinse water and recycling the slurry over the vibrascreens or the CPI.
6. The floc-clarifier system has the ability to clarify the process water and dewater the sludge.
7. Additional treatment of the clarified process water through polishing filters and activated carbon should allow, in most cases, reuse of this water for recycle to the washing circuit.
8. Side streams from the VRU will be treated using various physical/chemical extraction units currently under development by EPA.
9. The VRU offers a unique method for conducting treatability studies on various contaminated soils.

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GUIDANCE FOR TREATABILITY TESTING UNDER CERCLA: AN UPDATE

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ABSTRACT

The Risk Reduction Engineering Laboratory is working with EPA's Office of Emergency and Remedial Response to prepare guidance documents on the subject of treatability testing for Superfund sites. This paper describes a recommended approach to treatability testing in stages or tiers. Remedy screening, remedy selection and remedy design treatability tests are described. The paper also discusses technology specific treatability guidance documents that are in preparation. Technology specific documents address solidification of inorganics, soil washing, aerobic biodegradation (screening scale only), soil vapor extraction, and chemical dehalogenation. The documents present a structured, tiered approach unique to testing each technology and identify critical factors which must be evaluated during testing of these potential cleanup technologies.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

EPA's Office of Research and Development (ORD) has a long history of involvement in treatability study research for toxic chemicals. Much of that work has been in support of wastewater treatment regulations for both industrial and municipal systems. The goals of those studies can be classified as follows:

studies to determine the effectiveness of a specific technology/waste combination

studies to determine the effectiveness of a specific process(es) against one or more toxic chemicals (not from any particular source)

studies to optimize the performance of a particular technology/waste combination.

All of these goals apply to treatability testing under CERCLA. ORD's treatability experience is currently being applied and extended to the Superfund program in evaluation of remedial technologies for potential application at NPL sites. In fact, the primary goal of the Technical Support Branch of RREL is to provide expert advice on treatment technologies for specific NPL sites. Much of the assistance being given involves advice on use of treatability studies for evaluation of treatment alternatives.

This paper discusses the concept of treatability testing as applied to the Superfund program. The paper discusses the background of increased emphasis on treatability testing under CERCLA, the current status of treatability testing, and some of the problems in applying treatability tests in the Superfund scenario. It will give some specific examples of treatability tests and other related tools available to Regional Superfund programs.

## INHIBITIONS TO TREATABILITY TESTING

One of the criticisms of the EPA Superfund program has been that treatability studies are not conducted during the Remedial Investigation/Feasibility Study (RI/FS) time period of site remediation (1). The reasons for this situation can be easily understood. The strict deadlines on conducting RI/FS's do not encourage conducting treatability studies, which by their nature take time to plan and complete. The goal for completion of the RI/FS is 22 months. Several months are frequently necessary to get a preliminary idea of the problems presented at a site. It could be a year or more before adequate site contaminant data are available to enable a site manager to be in a position to commit to a treatability study. Furthermore, guidance on what constitutes adequate treatability testing under the Superfund program has been lacking. Among technology experts (both within and outside of EPA) there are differences of opinion as to how technologies should be evaluated.

An internal EPA review of the Superfund program has produced several recommendations regarding the use of innovative technologies and treatability testing:

Program guidance should ensure that treatment technologies are given stronger emphasis

EPA should establish technology support teams within the Office of Research and Development.

EPA should establish a treatability assistance program to perform treatability tests, develop standard testing protocols, and maintain a database of testing results. Guidance on how to use treatability tests in selecting clean-up technologies should be provided.

ORD should provide easier access to information on technology performance.

The Superfund Innovative Technology Evaluation (SITE) program (and other research programs) should be expanded to provide evaluations of innovative technologies and provide for rapid dissemination of results.

The focus of these recommendations is that innovative technologies should be investigated more thoroughly at Superfund sites and the use of treatability tests should be increased to evaluate treatment technologies scientifically before they are chosen for site remediation.

#### TREATABILITY GUIDANCE

One way that RREL has responded to the need for treatability study assistance is by production of guidance documents on the conduct of treatability studies. In December of 1989, RREL published "Guidance for Conducting Treatability Studies Under CERCLA" (2). This guide resulted from input from numerous individuals representing EPA's regional offices, contractors and technology vendors as well as from EPA's Office of Research and Development (ORD). The document describes the steps necessary to conduct treatability testing, from selecting technologies, issuing work assignments, to preparing workplan and QA plans. The document also describes how to use treatability results in the FS.

Remedial alternatives, under the CERCLA program, are evaluated against 9 criteria:

- Overall protection of human health and the environment
- Compliance with 'Applicable or Relevant and Appropriate Requirements' (ARARs)
- Implementability
- Reduction of toxicity, mobility, or volume
- Short-term effectiveness
- Cost
- Long-term effectiveness

Community acceptance  
State acceptance

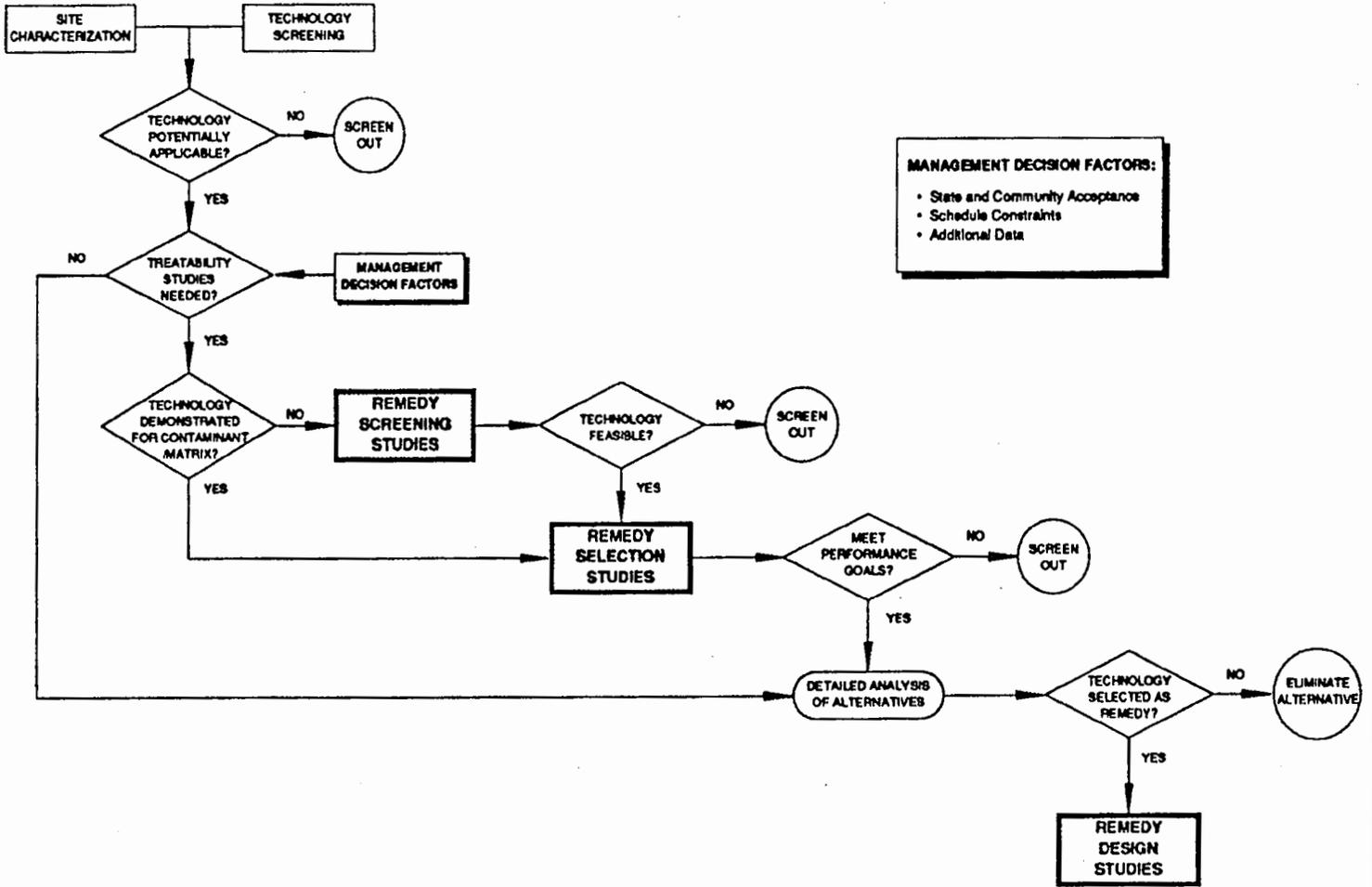
The 'guide' describes how treatability studies can help to address the first seven of these criteria. Traditionally, treatability studies have been used to determine the effectiveness of the technology in reducing contaminant levels or in meeting regulatory levels (which relate to Compliance with ARARS). However, the Superfund remedy evaluation process asks that treatability studies be formulated to answer much more comprehensive questions relating to issues such as cost, short and long term effectiveness and potential problems with implementability.

Recognizing the unique requirements of evaluating and selecting remedies under CERCLA, this guide presents a tiered testing strategy for conducting treatability tests and for incorporating treatability results into the remedy evaluation process (figure 1). Prescreening consists of literature reviews and consultation with technology experts to obtain an indication of whether the technology has been successfully applied in similar situations. In general, 'screening' level testing is used to provide a qualitative evaluation of the potential effectiveness of a technology. The remedy screening tier of testing is used to indicate whether further testing is warranted to more thoroughly evaluate a treatment technology or whether the technology should be screened out. In order to begin treatability testing as early in the RI/FS process as possible, remedy screening treatability tests are intended to be run based on minimal site information. In general, it is not necessary to have detailed data on contaminant levels and spatial distribution. Nor is it necessary to have in-depth data on site characteristics such as soil permeability or soil particle size distribution. This type of detailed data is usually not available in the early stages of site investigation but where needed, can often be generated as a part of treatability testing. Remedy screening treatability testing is designed so that a series of simplified tests are run which represent a range of process options within a technology class, such as 'biodegradation' or 'thermal treatment'.

'Prescreening' is an important step in the evaluation of treatment technologies and should precede treatability testing. The purpose of prescreening is to obtain an indication of whether the technology is potentially applicable to the situation in question and what scale of treatability testing, if any, is warranted. Literature reviews, database searches, vendors literature, and consultation with technology experts are all potentially valuable information sources which can be utilized during remedy prescreening.

Remedy screening treatability testing is characterized by relatively low cost and short time for completion. Remedy screening testing may not be necessary for situations where the performance of a technology is well documented with contaminants and matrices similar to those being considered. Remedy screening testing does not necessarily have to be conducted by a technology vendor. In general, remedy screening treatability tests are generic to a class of treatment technology and therefore can be done by any suitably equipped laboratory.

FIGURE 1 - Flow Diagram for Tiered CERCLA Treatability Testing



**MANAGEMENT DECISION FACTORS:**

- State and Community Acceptance
- Schedule Constraints
- Additional Data

The remedy selection tier of testing is used to provide data to support evaluation of a specific remedy in the FS. The remedy selection treatability test should provide performance data which will indicate whether ARARs or cleanup goals can be met at the site by the technology. Remedy selection treatability tests should also allow for estimation of costs associated with implementation of the remedy to the accuracy required for the FS (+50/-30%). Remedy selection treatability testing requirements vary depending on the technology being evaluated and on site specific factors. For some technologies, testing only at a laboratory bench scale may be sufficient to provide performance data adequate to meet the needs of the FS. In other cases, testing at both a bench and pilot scale may be required. Pilot scale testing will usually be necessary where it is difficult to simulate field conditions in the laboratory (e.g. in-situ treatment technologies). Where the types of experiments and equipment involved in remedy selection treatability tests are very specific to the treatment process, remedy selection testing will probably have to be conducted by the technology vendor. In other cases, where the treatment process could be carried out by a number of vendors and the treatment equipment is more commonly available (e.g. some types of incineration), remedy selection treatability testing could be conducted by any suitably equipped facility.

Remedy design treatability testing will usually be required after a record of decision has been issued. The purpose of remedy design testing is to optimize the selected treatment process and to obtain detailed cost and performance data. Remedy design testing is highly vendor specific and will usually be conducted by the vendor as a step in remedy implementation.

#### TREATABILITY TEST TIMING AND THE RI/FS PROCESS

This scenario for treatability testing has been devised to fit into the overall Superfund remedy evaluation process. For a specific site, numerous technologies can be pre-screened early in the RI/FS process based upon available information. Where adequate performance data are available for a treatment technology with similar waste material, remedy screening testing may not be necessary. Where there are significant concerns regarding the applicability of treatment technologies, screening tests can be conducted in a relatively short time period.

The Superfund program has targeted a 22-month RI/FS process. Included in this time period is initial site scoping, the field investigation (probably in at least two phases), preparation and evaluation of the remedial investigation report and the feasibility study, detailed analysis of remedial alternatives, and issuance of the record of decision.

Treatability tests have been formulated in a tiered approach that can be fit into such a schedule. Figure 2 illustrates where the treatability study tiers fit into the RI/FS process. To accomplish this, remedy screening treatability testing (if appropriate) must be started very early in the 22-month time period. However, usually at this early stage in site investigation, there are significant data gaps regarding site characteristics. Many of the site characteristics and measurement parameters which would enable experts to recommend potential treatment technologies will not be available.

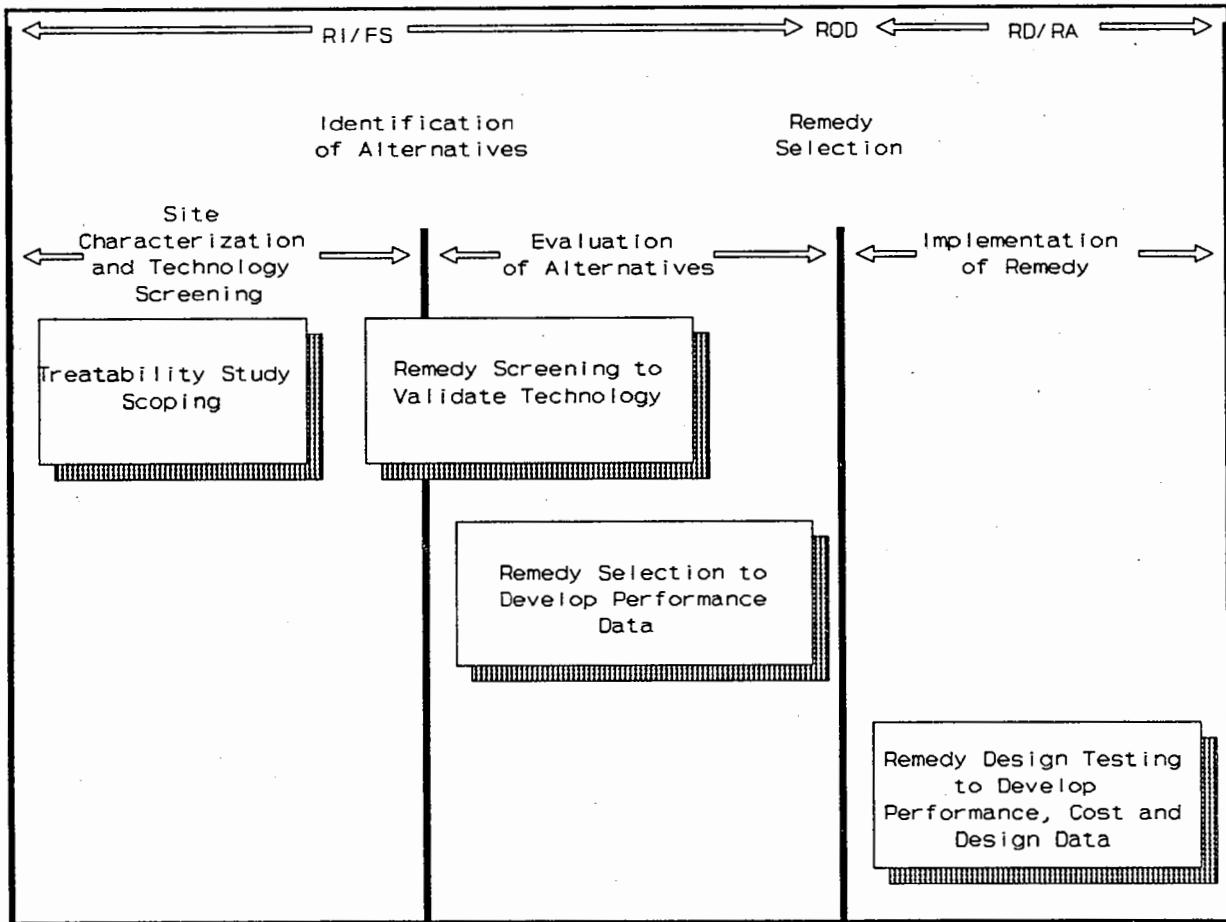


Figure 2 - Tiers of Treatability Testing in the RI/FS Process

Hence, in the past site managers were asked to conduct remedy screening treatability studies for a number of technologies and make selections based upon minimal information. Remedy screening treatability studies are being designed so that they are relatively inexpensive and reasonably quick to perform. Evaluation of a number of technologies at the screening level will provide a more scientifically supported selection of treatment technologies on which to conduct detailed testing.

When conducting screening treatability tests there is also a greater risk of both 'false positives' (deciding to conduct further testing on an inappropriate technology) and 'false negatives' (deciding that a technology is not appropriate for a site when in fact it is appropriate). By conducting a number of relatively inexpensive screening tests for a specific site, these risks of inappropriate decisions regarding treatment technologies at the screening level are acceptable when balanced against the savings of time and money.

The results of screening tests, coupled with additional information obtained during the RI may indicate that a treatment technology should proceed to remedy selection treatability testing. Although these tests are more time

consuming to conduct, in general, it should still be possible to conduct them within the RI/FS timeframe. The cost of remedy selection testing is justified considering the typical costs associated with site cleanups.

### TECHNOLOGY SPECIFIC TREATABILITY GUIDANCE DOCUMENTS

'A Guide for Conducting Treatability Studies Under CERCLA' presents a generic approach to conducting treatability studies for treatment technologies. The process of treatability testing consists of more than the actual experimental details of testing. In the Superfund program, treatability testing includes pre-screening of alternatives, planning treatability studies, the actual conduct of studies, as well as interpretation of treatability data and incorporation of that data into the analysis of alternatives. The guide defines treatability testing in the broad sense; considering steps necessary from initial site scoping through selection of a treatment technology in a Record of Decision.

Although the guide is comprehensive in dealing with a number of technical and administrative topics relating to treatability studies, by its nature it cannot deal in any depth with the technical details involved in testing a specific technology. For this reason, RREL is in the process of developing a number of guidance documents which deal with the testing of specific treatment technologies.

Shown in Table 1 are the documents which are currently under preparation. With the exception of the biodegradation guide, these documents are designed to assist in the conduct of treatability testing, from initial site scoping through final remedy selection. The biodegradation guide is only designed to include the steps necessary to screen aerobic biological degradation as a potential treatment remedy.

The guides are intended as management tools rather than cookbook 'protocols' for conducting treatability testing. While these guidance documents contain technical information necessary to conduct acceptable treatability experiments on a potential treatment technology, they also contain steps of a more administrative nature that are necessary in the conduct of treatability testing. Such steps include:

pre-screening the technology to determine whether it is potentially applicable at a site,  
 recommended content of a workplan that would be prepared to plan treatability testing,

<u>Technology</u>	<u>Publication Expected</u>
Soil Washing	March 1991
Stabilization of inorganics	Dec 1991
Aerobic Biodegradation *	Feb 1991
Soil Vapor Extraction	June 1991
Chemical Dehalogenation	April 1991
Solvent Extraction	Dec 1991
Thermal Desorption	Dec 1991

\* Screening level only

interpretation of treatability testing data and incorporation of that data into the feasibility study analysis of alternatives.

All of the technology specific guides being prepared are being formatted similarly. A common format (Table 2) was designed for these guides so that the user can consult that portion of the guide which is needed at a particular point in time (i.e. when preparing or reviewing a workplan for a treatability study).

In developing these guidance documents, a common approach has proven useful. Early in the development stages of each document, a workgroup was conducted to get input on how treatability tests are conducted with the technology chosen. For this

workgroup meeting, a 'strawman' treatability guide was prepared. This 'strawman' document was useful in giving workgroup attendees something to focus constructive comments. We attempted to get workgroup participation from a number of interested sources including EPA's Regions, EPA's Office of Solid Waste and Emergency Response (OSWER), ORD/RREL, academia, consulting firms and technology vendors. Participation by Regional RPMs and technology vendors has been particularly useful in learning the experiences gained in the actual conduct of treatability studies in CERCLA and other programs. In getting technical reviews of the various drafts of each treatability guide, we attempted to solicit comments from as broad a group as possible.

During the development of these documents, a number of facts became apparent and shaped the thinking on the 'prescriptiveness' of these documents. First, in the expert workgroup meetings which were held to gain input for these documents, it was apparent that those experts who are currently doing treatability testing on treatment technologies have different (and equally valid) methods of conducting that testing. Although experts generally agreed on the critical parameters that need evaluation for a particular technology, their approach to investigation of those parameters varied.

Secondly, the database of treatability study results is not of sufficient magnitude to be able to recommend a 'standard treatability protocol' which would lead to optimum technology evaluation in all cases. The

**TABLE 2 - OUTLINE FOR TECHNOLOGY  
SPECIFIC TREATABILITY GUIDANCE  
DOCUMENTS**

**INTRODUCTION**

- Background
- Purpose and scope
- Intended audience
- Use of the guide

**TECHNOLOGY DESCRIPTION & PRELIMINARY SCREENING**

- Technology description
- Pre-screening the technology

**THE USE OF TREATABILITY TESTS IN REMEDY SELECTION**

- The Process of treatability testing in selecting a remedy
- Applicability of treatability tests

**TREATABILITY STUDY WORK PLAN**

**SAMPLING AND ANALYSIS PLAN; QUALITY ASSURANCE PROJECT PLAN**

**TREATABILITY DATA INTERPRETATION**

- Technology evaluation
- Estimation of costs

experts have agreed that a considerable amount of professional judgement is necessary in formulating a treatability test which incorporates site specific factors and circumstances.

Lastly, the details of treatability testing are highly matrix and process dependent. In order to make the guidance documents broad enough to cover more than one specific process and matrix, a degree of flexibility in the details of experimentation is needed. As an example, biological treatment can be applied to various media such as liquid, sludges, soils, or sediments. Biological treatment can also be applied via a number of processes such as slurry biodegradation or composting. The details of experimentation with each of these process/matrix combinations are different.

Therefore, the final versions of these documents have been constructed to be flexible enough to allow professional judgement in formulating treatability test plans and to allow for variations in treatability test methodology. The documents concentrate on formulating a tiered approach to testing with that technology and on identifying critical factors which need to be investigated in each of those tiers. The documents, in many cases, present options for investigating those critical factors, but the selection of the appropriate option depends on the specific circumstances at a site and should be left to those more familiar with the site.

#### AEROBIC BIODEGRADATION - REMEDY SCREENING

This guide describes the screening tier of testing only and, therefore, would not by itself lead to selection of a biological treatment remedy. Such remedy selection guidance will be forthcoming at a later date.

The main determining factor in pre-screening site/matrix combinations for potential for aerobic biodegradation is literature review for the degradability of the compounds (or similar compounds) at the site. There are site factors which may ultimately preclude biodegradation at a site (such as extreme pH or concentrations of contaminants which are toxic to the degrading organisms), but it may be possible to negate these factors by various pretreatment methods. These methods would be explored in the remedy selection tier of testing.

This guide discusses the important aspects of screening testing. Aliquots of soil from a site are placed in soil reactors.

**REMEDY SCREENING AEROBIC  
DEGRADATION TREATABILITY  
TESTS**

Prescreening - Literature review for biodegradability of contaminants of concern or similar compounds. Some site conditions such as extreme pH or activity inhibiting concentrations can be 'engineered'.

Remedy Screening - Jars or flasks containing soil can be either saturated or unsaturated. Nutrients and/or micro-organisms can be added. Reactors sampled periodically to assess contaminant loss. Sterile controls used to assess abiotic losses. Volatility can be assessed by off-gas sampling, but usually deferred to remedy selection testing. Screening is 'successful' if 20-50% degradation observed.

	<u>Lab Test Time</u>	<u>Cost</u>
Remedy Screening	20-30 weeks	\$10K-50K

One aliquot is initially analyzed for a baseline contaminant level and additional aliquots are analyzed at later times to estimate the degree of degradation. 'Sterile controls' (it is difficult to sterilize soil) are recommended so that degradation due to abiotic mechanisms can be taken into consideration. If volatile compounds are present, analysis of off-gas can be conducted, but is not routinely recommended for the screening level of testing. The main question to be answered at a screening level of testing is whether further testing is warranted to evaluate a potential biological treatment remedy in more detail. Therefore, the goal of screening biological testing is not whether contaminants are reduced to a 'cleanup level', but rather to demonstrate that biodegradation is taking place. The guide proposes that if 20%-50% degradation is detected, then further testing at a remedy selection tier may be warranted.

## SOIL VAPOR EXTRACTION

The screening tier of treatability testing for SVE involves the use of soil columns composed of soil from the site. This guide draws heavily from guidance and experience developed as a part of Leaking Underground Storage Tank research. This guide discusses pre-screening site characteristics to determine whether the vapor pressure of contaminants of concern are greater than 0.5 mm Hg.

Screening tests with soil columns are run for a short time to determine whether contaminants are being removed. In many cases, screening testing may not be necessary for SVE if the vapor pressure of the compounds of concern are significantly above 0.5 mm Hg. Screening testing may be warranted where the vapor pressure of the compounds of concern is near 0.5 mm Hg or where the soil from the site appears to be very non-permeable.

The remedy selection tier of testing for SVE consists of at least 3 parts: 1) column tests, 2) field air permeability measurements, and 3) mathematical modelling. In some cases (i.e. complex sites or where bedrock contamination exists), pilot scale testing may be necessary for remedy selection. Column testing for SVE remedy selection treatability studies provides information regarding the ultimate cleanup level that can be expected from the technology. It also provides an estimate of the effective Henry's law constant for use in mathematical modelling. Field air permeability measurements are used to

### SOIL VAPOR EXTRACTION TREATABILITY TESTING

Prescreening - SVE is potentially applicable where contaminant vapor pressure is > 0.5 mm Hg

Remedy Screening - Laboratory column tests can give an indication of removal rates, but are not truly representative of in situ conditions.

Remedy Selection - Column tests indicate the ultimate cleanup level potentially achievable. Field air permeability measurements aid in modelling air movement through soil. Mathematical modelling predicts cleanup time/cost. Field pilot testing may be necessary for complex sites or sites with bedrock contamination.

	Lab Test Time	Cost
Remedy Screening	~2 weeks	\$10-\$50K
Remedy Selection		
Column Tests	3-7 weeks	\$30\$-70K
Air Permeability	1-5 days	\$10-\$50K
Modelling	1-2 weeks	\$10-\$20K
Pilot Tests	1-3 months	\$100K+

obtain data on the permeability of the site so that air movement underground can be modelled. Mathematical models use data from both the column tests and air permeability tests to estimate the time for site remediation and associated construction and operating costs.

## CHEMICAL DEHALOGENATION

Chemical dehalogenation involves addition of a chemical reagent to contaminated material (soil, sludge, liquid). The reagent effects the removal of one or more halogen atoms from the contaminant molecule. The technology is applicable to dioxins, PCBs, some chlorinated pesticides and other halogenated carbon compounds. The technology is generally best suited to situations where contaminant concentrations are at ppm levels or greater. For soils and sludges, the total waste volume should be greater than  $\sim 1000 M^3$  to be cost effective.

Remedy screening for this technology involves treatment tests on a 'worst case' sample of the matrix to be treated. Remedy screening tests are conducted in the laboratory under the most favorable conditions for dehalogenation. Since chemical dehalogenation processes vary among vendors, the most favorable conditions will be process dependent. Typical conditions would involve an excess of reagent, relatively high temperatures and process treatment times. The goals for remedy screening testing are to achieve  $\sim 90\%$  reduction (or the cleanup goals if known) in the contaminant concentration.

Remedy selection treatability testing for chemical dehalogenation involves the same physical scale of test equipment. However, the goal of remedy selection treatability testing is to optimize the treatment conditions to the contaminant/matrix combination(s). Treatment residuals are analyzed to verify that they meet the cleanup goals. Toxicity testing is also done on treatment residuals to verify that overall toxicity is reduced. The optimized treatment conditions allow for estimation of costs for the full scale remedy (sufficient to meet RI/FS cost criteria).

## SOLIDIFICATION/STABILIZATION OF INORGANICS

Stabilization of inorganics (toxic metals and some inorganic compounds) is an accepted developed technology for many metals. In some cases a screening level treatability test can be waived if sufficient data exists for treatment of the same form of the specific target metals in similar soil

CHEMICAL DEHALOGENATION TREATABILITY TESTING		
<u>Prescreening</u>	- Applicable to halogenated aromatics and aliphatics (PCBs, dioxins/furans, chlorophenols, ethylene dibromide). Most cost effective for volumes $> 1000 M^3$ .	
<u>Remedy Screening</u>	- Bench scale test under conditions of most likely success. Success indicated by 80-90% contaminant reduction.	
<u>Remedy Selection</u>	- Optimization of process/reagent at bench scale. Toxicity testing recommended on treated soil.	
	<u>Lab Test Time</u>	<u>Cost</u>
Remedy Screening	$\sim 2-5$ days	\$10-\$50K
Remedy Selection	$\sim 3-6$ weeks	\$20-\$100K

matrices. However, for other inorganics (i.e. arsenic, mercury, and inorganic compounds) or for differing ionic forms of compounds, a screening level study is recommended. The screening level study is generally done using several mixtures of generic reagents including portland cement, fly ash, and clays. Results are evaluated using both destructive (TCLP) and non-destructive (ANS 16.1) leaching tests along with measurements of permeability and unconfined compressive strength.

Remedy selection treatability testing is conducted in a similar manner but involves more intensive testing including more samples, quality assurance and more analysis of stabilized product. A tiered approach is preferred. Results from the first round of tests on various mixtures and ratios of reagents leads to a second round of more intensive testing on the particular mixture and ratio of reagents that performed well in the initial tier. For more difficult to stabilize metals (i.e. arsenic or mercury) or inorganic compounds, vendor specific reagents and procedures may be necessary to adequately evaluate the effectiveness of the technology. Although not included in this particular document, it appears that stabilization of many semi-volatile organic compounds can also be accomplished by use of vendor specific treatment technologies. A treatability guide specific to evaluating stabilization of organic compounds is being considered for a future publication.

## SOIL WASHING

The screening tier of treatability testing for Soil Washing involves the use of jar tests with soil from the site. Screening tests are run for a short time period (less than 1 week) to determine whether contaminants are being removed. In some cases, screening tests may not be necessary for soil washing if the identities of the compounds of concern and the physical and chemical characteristics of the soil indicate the technology may be successful at a site.

The remedy selection testing tier for soil washing consists of bench-scale wet-sieve tests. They yield data which verify that the technology can meet expected cleanup goals, provide information in support of the detailed analysis of alternatives, and give an indication of optimal operating conditions. Toxicity testing is also performed on treatment residuals. The optimized operating conditions allow for estimation of cost for the full-scale remedy.

### STABILIZATION OF INORGANICS TREATABILITY TESTING

**Prescreening** - Applicable to metals for which a substantial data base on successful application exists.

**Remedy Screening** - Bench scale test for metals and inorganic compounds for which a substantial data base of successful treatment does not exist. Can be skipped for commonly stabilized contaminant/soil types.

**Remedy Selection** - Tiered optimization of reagent and mixture ratios at bench scale using vendor specific technology for the more difficult to stabilize inorganics.

	<u>Lab Test Time</u>	<u>Cost</u>
Remedy Screening	2-3 months	\$10-\$50K
Remedy Selection	3-6 months	\$50-\$150K

## SUMMARY

A tiered approach has been described that can be used in evaluating alternative technologies applicable to Superfund wastes. This approach will aid in obtaining defensible data in support of remedies selected at Superfund sites. In addition to general guidance on the conduct of treatability studies, EPA-RREL is preparing technology specific guidance documents which will help in evaluating the applicability of those technologies at sites. These documents describe how to prescreen the technology for potential applicability, important factors to consider in conducting tests and how to interpret and use treatability data in the Superfund remedy evaluation process.

### SOIL WASHING TREATABILITY TESTING

Remedy Screening - Laboratory jar tests can give a preliminary indication of removal efficiencies, but are not normally used. The contaminant identity and physical and chemical characteristics of the soil can usually be used to predict the potential success of soil washing.

Remedy Selection - Bench-scale wet-sieve tests indicate ultimate cleanup levels potentially achievable. Optimization of process/reagent is done at the bench level.

	<u>Lab Test Time</u>	<u>Cost</u>
Remedy Screening	~2-5 days	\$10-\$50K
Remedy Selection	~3-6 week	\$20-\$100K

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S.I.T.E. DEMONSTRATION OF A SOIL WASHING SYSTEM  
BY BIOTROL INC., AT A WOOD PRESERVING SITE  
IN NEW BRIGHTON, MINNESOTA

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ABSTRACT

A pilot scale demonstration of BioTrol, Inc.'s Soil Washing System (BSWS) was conducted under the U.S. EPA's Superfund Innovative Technology Evaluation (SITE) Program, at a Superfund site in New Brighton, Minnesota. The BSWS treated soils contaminated with wood treating wastes, including creosote-fraction polynuclear aromatic hydrocarbons (PAHs) and pentachlorophenol (penta).

In the SITE Program test, the component technologies of the BSWS were the Soil Washer (SW), Aqueous Treatment System (ATS), and Slurry Bio-Reactor (SBR). The demonstration determined the contaminant reduction efficiency of all three BioTrol technologies. Also, a material balance was determined for the penta and PAHs in the Soil Washer. A 2-day test used 200 ppm penta soil, with similar total PAH concentrations, and a 7-day test used 1000 ppm penta and PAH soil. The equipment ran 24 hrs/day.

The SW separates the relatively clean sand fraction (roughly two-thirds by weight of the soil) from the highly contaminated silt and clay fractions, by intensive scrubbing and size classification. The remaining contaminated silt/clay slurry was treated in the SBR. Contaminated process water from the SW was treated in the ATS. The ATS is a microbiological system for degrading toxic organics in water. It consists of naturally occurring microbes growing on a plastic matrix in tanks, which degrade penta and PAHs into harmless carbon dioxide, water, and inorganic chloride. The SBR is a three-stage microbiological system for degrading organics on slurries of soil fines, consisting of three upright, continuously-stirred reactors. The results will be available once laboratory analyses are complete.

This paper has been reviewed in accordance with the U.S. Environmental

Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

A pilot scale demonstration of the BioTrol Soil Washing System (BSWS) was conducted under the U.S. Environmental Protection Agency's (EPA's) Superfund Innovative Technology Evaluation (SITE) Program from September 25 to October 16, 1989, at the MacGillis & Gibbs Superfund site in New Brighton, Minnesota. In this test, the three component technologies of the BSWS were: the Soil Washer (SW), Aqueous Treatment System (ATS), and Slurry Bio-Reactor (SBR). Soils were treated that were contaminated with wood treatment process wastes, including creosote-fraction polynuclear aromatic hydrocarbons (PAHs) and pentachlorophenol (penta).

### SITE Demonstration of the BioTrol Soil Washing System (BSWS)

This SITE demonstration evaluated the soil washing system developed by BioTrol, Inc., of Chaska, Minnesota. The object of this demonstration test was to determine if the concentrations of penta and creosote-fraction PAHs in the soil entering the SW, the water entering the ATS, and in the slurry entering the SBR, could each be reduced by at least 90 percent in the respective effluents. A second objective was to determine the fate of penta and PAHs by material balance calculations for the SW, to assure that the measurements of reduction efficiencies were not affected by uncontrolled material losses to the environment.

Science Applications International Corporation (SAIC) assisted the EPA in conducting the demonstration test, handling community relations, disposing of residuals generated by the test, and preparing the final test report. The analytical laboratories of Acurex Corporation, Radian Corporation, and SAIC analyzed samples from the demonstration test. BioTrol worked with the EPA and SAIC by providing input to the design of the demonstration test, and providing all necessary equipment and manpower for demonstration of the BSWS.

### The BioTrol Soil Washing System

The SW operates on the principle that a significant fraction of the chemicals in a contaminated soil are either physically or chemically bound to the silt, clay or humic particles, and removal of these fine particles leaves the bulk portion of the soil (mostly sand) relatively clean. Figure 1 is a simplified diagram of the SW. Excavated soils are screened to remove debris and mixed with water to form a slurry. The slurry is

subjected to a series of intensive scrubbing and physical classification steps to scour the contaminants and silt and clay fines from the sand particles. The washed sand is separated from the slurry, and the remaining contaminated fines can be treated in the SBR. Contaminated process water from the SW can be sent to the ATS to remove penta and PAHs.

The ATS is a microbiological system for degrading toxic organics in contaminated water. It consists of naturally occurring microbes growing on plastic support material in tanks. Figure 2 is a simplified diagram of the ATS. The SW effluent process water's pH is adjusted and nutrients are added to optimize the performance of the ATS microbes. Next, BioTrol adds a specific, naturally occurring microorganism to the microbes already present in the SW effluent. This combination of microbes rapidly degrades the penta and PAHs into carbon dioxide, water, and inorganic chloride, which are harmless products<sup>1-3</sup>.

The SBR is a three-stage microbiological system for treating degradable organic contaminants associated with the fine soil particles. The equipment used in the demonstration was a pilot-scale EIMCO BioLift™ reactor system manufactured by the EIMCO Process Equipment Company. BioTrol uses the SBR to remove contamination from the clay and silt discharged by the SW. The SBR consists of three upright, continuously stirred reactors, each with a capacity of 60 L. Figure 3 is a simplified diagram of the SBR. The silt and clay slurry enters the first reactor where the degradation of organic contaminants by the pre-inoculated microbe population begins. As the slurry flows to each successive tank, the contaminants are further degraded to inorganic products.

### The Test Site

The MacGillis & Gibbs Company has operated a wood treatment facility on this site since about 1920. Contaminants present at the site include creosote, penta, and chromated copper arsenate (CCA)<sup>4</sup>. Creosote was used as a wood preservative from about 1920 until about 1950. During the late 1940s the MacGillis & Gibbs Company began using a 5-percent mixture of penta in fuel oil. Penta was phased out in the mid-1970s and replaced by CCA. The MacGillis & Gibbs site was placed on the National Priorities List (NPL) in conjunction with the neighboring Bell Lumber and Pole site in September 1983 because of surface and groundwater contamination.

The site is underlain by the New Brighton Formation, consisting of silty, fine to medium grained sands with intermediate and laterally discontinuous silt and sand lenses. Processed penta waste had been placed into the disposal area, from which contaminated soil was obtained for the

demonstration test. The soil is particularly amenable to soil washing because of the high proportion of sand.

## DEMONSTRATION TEST DESIGN

### Test Plan

Two demonstration tests were conducted. For the first test, the SW ran for 2 days, using the low penta concentration soil (100-200 ppm), and the ATS ran for about 4 days, but starting a day later than the SW. The second test included all three BSWs technologies, using high-penta soil (500-1000 ppm) from the disposal area, and lasted 7 days. On the fourth day of the high-penta soil test, the SW continued to operate, but 2,000 L of fine particle slurry from the thickener was diverted to a holding tank as feed for the two-week SBR test.

During the low-penta test, contaminated SW process water from the low concentration soil test was treated by the ATS. Automatic composite samples of the ATS system influent and effluent were collected. During the high-penta test, the contaminated water from the SW was treated in the ATS and recycled to the SW. Sampling of the ATS influent and effluent continued until all process water generated by the SW was treated. Solids released from the ATS on the last day of testing were collected in a bag filter. A carbon canister collected exhausted mists and vapors from the ATS during the test.

For the SBR test, manual composite samples of the input and output streams were collected beginning about two system retention times (2 x 5 days) after the start of continuous operation. The SBR effluent slurry was collected in a drum for eventual dewatering and disposal. A carbon adsorption canister was used to collect any fugitive emissions from the SBR.

## RESULTS

### The Soil Washer

#### Low-Penta Soil Test--

Table 1 shows the concentrations of penta in the feed soil and the effluent streams from the soil washer. The mass balance of solid and water streams for the low-penta soil test showed a 4 percent deficit in the output relative to the input, a minor discrepancy. The penta mass balance, however, showed a 40 percent gain in the output streams relative to input

streams. The possible reasons for this large discrepancy, in which the input mass of penta was probably undervalued, are discussed in the Conclusions section. The following performance results are corrected based on the Total Effluent penta as correct, and assume no gain relative to Total Influent penta.

With 176 mg/kg penta (corrected) in the feed soil, the washed soil showed 12.3 mg/kg, a 93 percent decrease in penta concentration for that soil fraction relative to the whole feed soil. The penta in the fine particle cake was 310 mg/kg. Thus, 3 percent of the effluent mass contained 37 percent of the penta. In comparison, the washed soil contained only 8 percent of all penta in output streams. The fine oversize and coarse oversize effluent streams together accounted for 16 percent of the penta, and the combined dewatering effluent accounted for the rest, 39 percent (treated in the ATS).

Seven PAHs were detected in the feed soil, at levels of 5-140 mg/kg, and totaling 240 mg/kg. Levels of 25 mg/kg total PAHs were found in the washed soil, while 700 mg/kg of PAHs was found in the fine particle cake. The contamination reduction for the washed soil was 90 percent.

#### High-Penta Soil Test--

Table 2 shows the concentrations of penta in the feed soil and the effluent streams from the soil washer. The mass balance of solid and water streams for the high-penta soil test showed a 4 percent increase in the output relative to the input, a minor discrepancy. The penta mass balance, however, showed a 50 percent gain in the output streams relative to input streams. The possible reasons for this large discrepancy, in which the input mass of penta was probably undervalued as in the low-penta test, are discussed in the Conclusions section. The following performance results are corrected based on the Total Effluent penta as correct, and assuming no gain or loss relative to Total Influent penta.

With 980 mg/kg penta (corrected) in the feed soil, the washed soil showed 85.7 mg/kg, a 91 percent decrease in penta concentration for that soil fraction relative to the whole feed soil. The penta in the fine particle cake was 1290 mg/kg. Thus, 3 percent of the effluent mass contained 29 percent of the penta. In comparison, the washed soil contained only 11 percent of all penta in output streams. The fine oversize and coarse oversize effluent streams together accounted for 30 percent of the penta, and the combined dewatering effluent accounted for the rest, 30 percent (treated in the ATS).

Nine PAHs were detected in the feed soil, at levels of 15-70 mg/kg. The total concentration of PAHs in the feed soil was 340 mg/kg. The PAHs showed 83-93 percent decrease in the washed soil. The total concentration of PAHs in the fine particle cake was 970 mg/kg, or 285 percent higher than in the feed soil.

### The Aqueous Treatment System

The ATS operated at a 11 L/min rate during the test, corresponding to a 3 hr residence time. The ATS showed a mean decrease of penta in the Low Soil Test from 13 mg/L to 1.4 mg/L, an 89 percent removal of penta.

For the High Soil Test, penta levels decreased from a mean of 41 mg/L to a mean of 2.2 mg/L, a 94 percent removal of penta.

The levels of all PAHs were below detection limits for most influent and effluent samples in both the Low and High Soil Tests, so a percent removal efficiency could not be calculated.

### The Slurry Bio-Reactor

The SBR showed an increasing efficiency in penta degradation, both in the aqueous phase and in the wet solids, up to the end of the 14-day test. The penta degradation in the aqueous fraction was 91 percent on day 11 (relative to day 6 influent, since the SBR residence time was 5 days), and 97 percent on days 12-14. The solids cake, from lab filtration of the influent and effluent slurries, showed the following efficiencies for days 11-14: 65, 61, 79, 92 percent.

Only three PAHs were detectable in both influent and effluent, and they showed a trend toward higher removal efficiencies near the end of the test. Comparing day 14 effluent to day 9 influent, removals for chrysene, fluorene, and pyrene were 86-99 percent.

## CONCLUSIONS

The BSWS is a combination of three effective treatment processes for organic hazardous waste. The SW uses water for leaching some of the water soluble penta, which is subsequently mineralized biologically in the ATS. The SW also accomplishes separation of the large, relatively clean sand fraction from the highly contaminated fine particles (mostly silt and clay) and from the coarse and fine oversize particles by scouring and size classification processes.

The efficient separation of the relatively clean washed soil fraction (predominantly sand) from the other solid fractions is a useful waste volume reduction process for contaminated soil cleanup. The fine and coarse oversize were woody material, mainly chips and sawdust, with a significant BTU value if dried before incineration. The fine particle cake was a concentrated, highly contaminated waste which can also be treated by incineration, or treated in the SBR. The SBR was quite efficient in treating a slurry of the fine particle fraction, removing both penta and PAHs. The ATS efficiently degrades penta in the combined dewatering effluent, removing the penta solubilized in the SW, and allowing the water to be reused.

The increase in the total mass of penta in the effluents relative to influents may be caused by poor extraction recoveries of penta during the analysis of the feed soil. The particle size separation and abrasion in the presence of surfactants during the soil washing may free penta from the matrix, making it more extractable in the effluent samples.

The MacGillis & Gibbs site is one of 54 wood preserving sites currently listed on the NPL. The BioTrol soil and water treatment technologies are potentially applicable to cleaning up these sites, as well as other sites with soil and water contaminated by organics. For sites where the contaminants would not be readily biodegraded, the SW could perform waste volume reduction, to reduce the cost of subsequent treatment and disposal options for the contaminated aqueous and fine fractions.

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Table 1. Soil Washer Mass Balance Results: Low-Penta Soil Test

	Influent & -- Effluent Mass --		----- Penta -----		
	kg	Percent	Concen- tration (mg/kg)	Total (g)	Percent of Total In or Out
<b>INFLUENTS:</b>					
Feed Soil	11,210	14%	126	1,412	100%
Municipal Water	61,710	79%	0	0	
Flocculant Solution	4,914	6%	0	0	
<b>TOTAL INFLUENTS</b>	<b>77,830</b>	<b>100%</b>		<b>1,412</b>	
<b>CORRECTED TOTAL PENTA*</b>				<b>1,976</b>	
<b>CORRECTED FEED SOIL PENTA**</b>			<b>176</b>		
<b>EFFLUENTS:</b>					
Washed Soil	12,940	17%	12.3	159	8%
Fine Particle Cake	2,374	3%	308	731	37%
Fine Oversize	653	1%	101	66	3%
Coarse Oversize	1,594	2%	162	258	13%
Combined Dewatering Effluent	56,850	76%	13.4	762	39%
<b>TOTAL EFFLUENTS</b>	<b>74,410</b>	<b>100%</b>		<b>1,976</b>	<b>100%</b>
<b>Gain or Loss</b>	<b>- 3,420</b>	<b>- 4%</b>		<b>+ 564</b>	<b>+ 40%</b>

\* Based on total effluent penta.

\*\* Based on corrected total influent penta and Feed Soil mass.

Table 2. Soil Washer Mass Balance Results: High-Penta Soil Test

	Influent & Effluent Mass		Penta		
	kg	Percent	Concentration (mg/kg)	Total (g)	Percent of Total In or Out
<b>INFLUENTS:</b>					
Feed Soil	17,590	16%	650	11,430	98%
Municipal Water	4,182	4%	0	0	
ATS Treated Water	73,550	68%	2.65	195	2%
Flocculant Solution	13,450	12%	0	0	
<b>TOTAL INFLUENTS</b>	<b>108,800</b>	<b>100%</b>		<b>11,620</b>	<b>100%</b>
<b>CORRECTED TOTAL PENTA*</b>				<b>17,240</b>	
<b>CORRECTED FEED SOIL PENTA**</b>			<b>980</b>		
<b>EFFLUENTS:</b>					
Washed Soil	22,860	20%	85.7	1,959	11%
Fine Particle Cake	3,931	3%	1290	5,071	29%
Fine Oversize	1,007	1%	932	939	5%
Coarse Oversize	3,132	3%	1370	4,291	25%
Combined Dewatering Effluent	82,300	73%	62.8	5,168	30%
<b>TOTAL EFFLUENTS</b>	<b>113,200</b>	<b>100%</b>		<b>17,430</b>	<b>100%</b>
<b>Gain or Loss</b>	<b>+ 4,400</b>	<b>+ 4%</b>		<b>+ 5,810</b>	<b>+ 50%</b>

\* Based on total effluent penta, with ATS Treated Water penta subtracted.

\*\* Based on corrected total influent penta and Feed Soil mass.

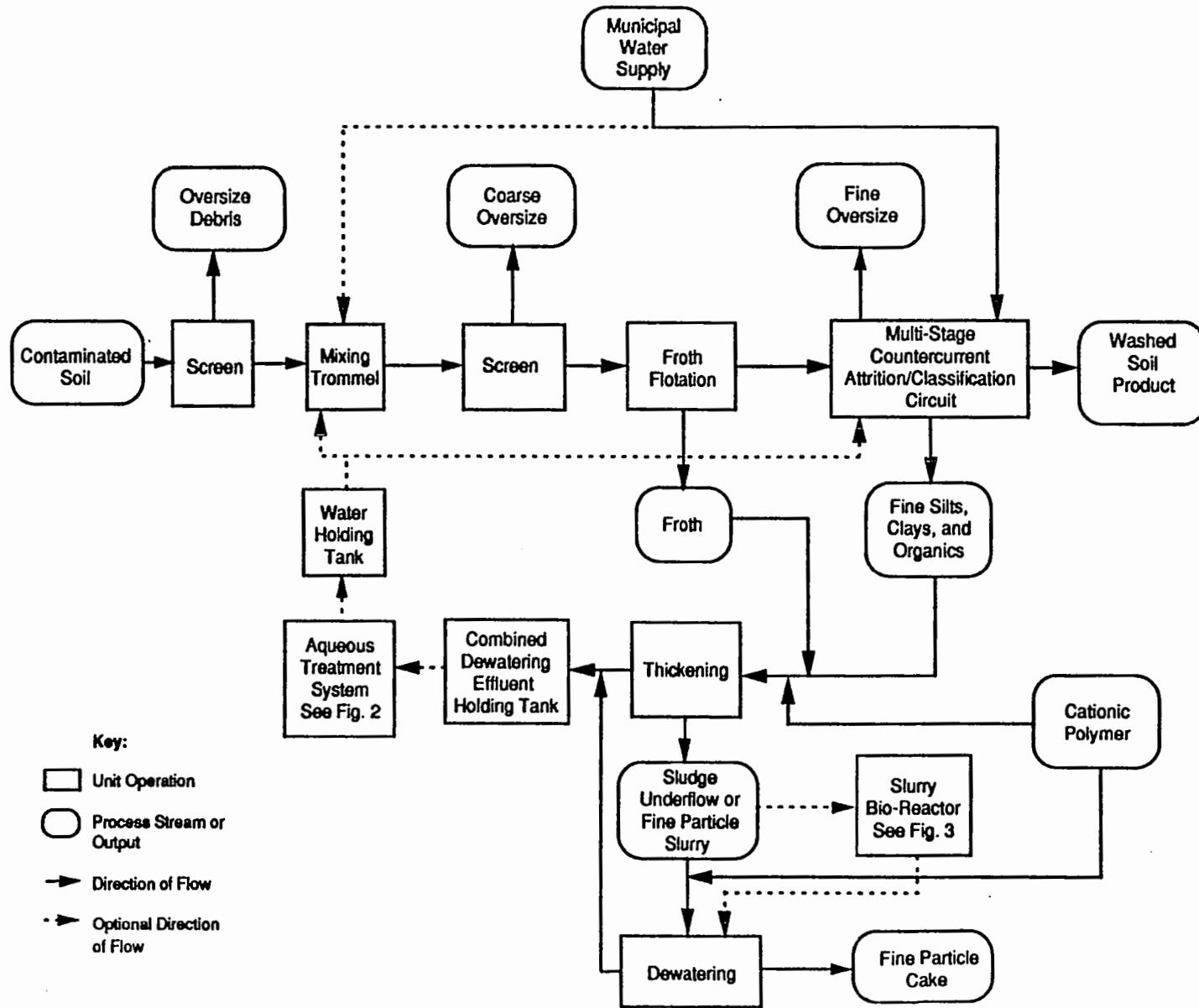


Figure 1. Flow Diagram of the Soil Washer (SW)

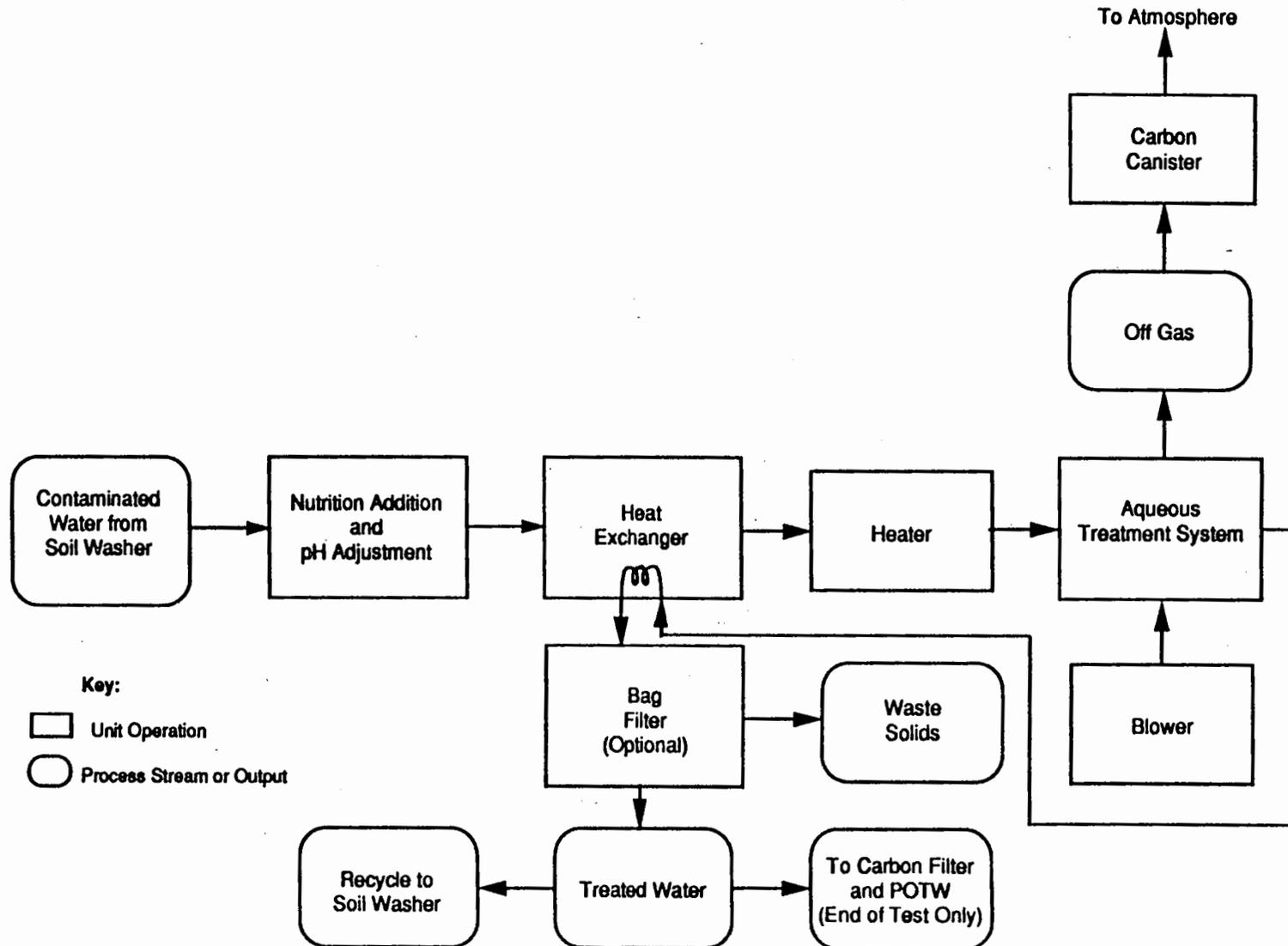


Figure 2. Flow Diagram of Aqueous Treatment System (ATS)

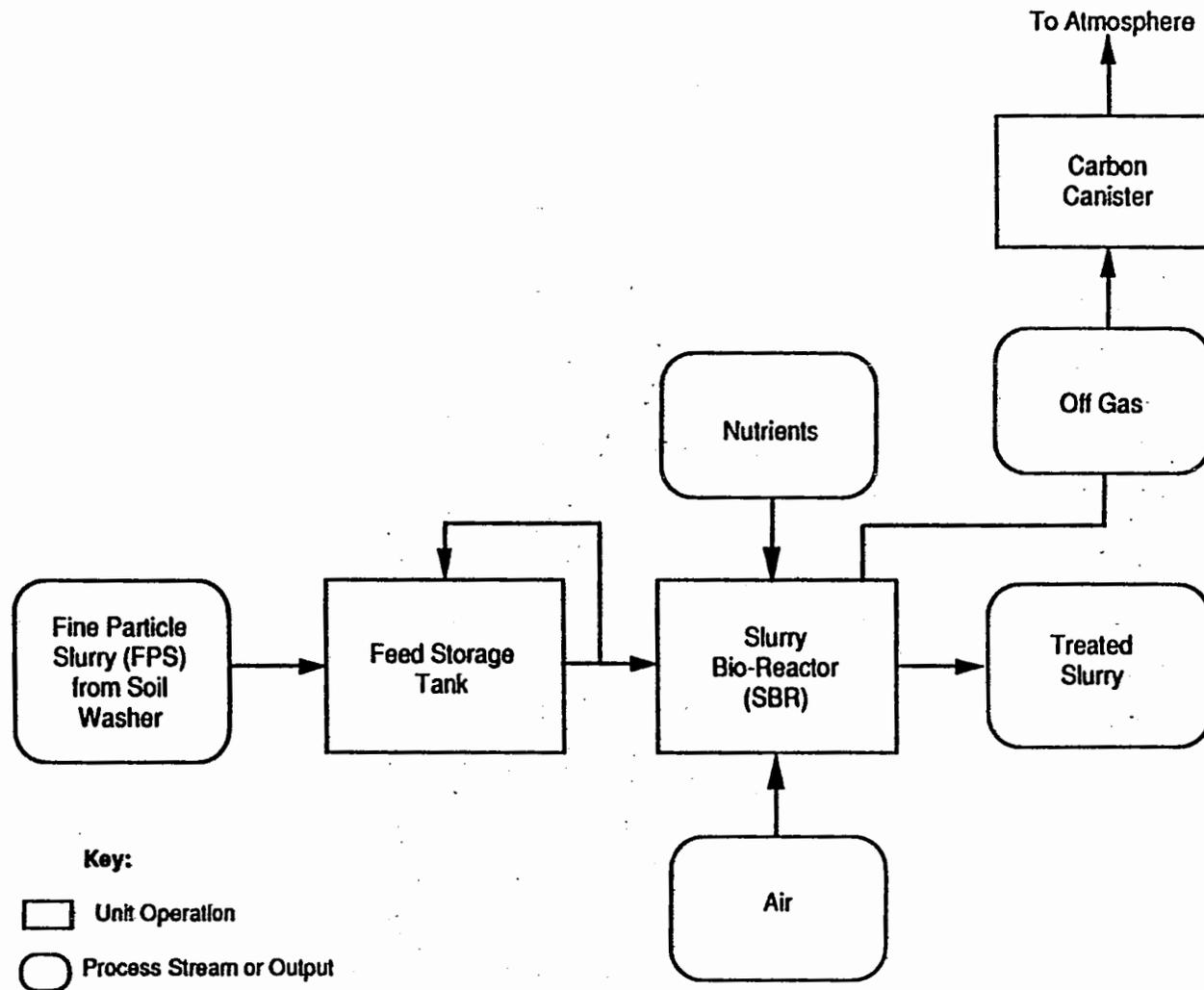


Figure 3. Flow Diagram of the Slurry Bio-Reactor (SBR)

**BACKGROUND INFORMATION ON CLEAN PRODUCTS**  
**RESEARCH AND IMPLEMENTATION**

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**ABSTRACT**

The concept that products can be made "environmentally friendly" or "clean" has been attracting much attention. However, there is as yet no accepted definition of what is meant by "environmentally friendly," nor any agreement on how to achieve clean products. This paper provides information on the current state of research and implementation on clean products and identifies issues to be resolved. The focus is on consumer products, although the same criteria and methodologies can be used for any product or process.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## THE LIFE CYCLE OF PRODUCTS

The manufacture, use, and disposal of products can impact on resources and the environment at every stage in the product's life cycle. The life cycle of a product moves from extraction of raw materials to processing stages and on through manufacture. The product then goes through the distribution channels to the consumer. Finally the product is consumed, disposed of, or perhaps recycled.

While there is general agreement that it is desirable to minimize a product's overall impact on resources and the environment, it is not so easy to determine what the impacts really are and how one product compares to another. Many claims that a given product is "environmentally friendly" are based on only one of the many possible points or types of impact on the environment.

### EXISTING AND PROPOSED CLEAN PRODUCTS PROGRAMS

Existing labeling programs (Figure 1) range from well-controlled national programs and simple shopping guidelines recommended by various consumer/environmental groups to labeling claims with undefined technical basis made by manufacturers and retailers trying to cash in on consumers' rising environmental concerns.

#### GERMANY: BLUE ANGEL

The Federal Republic of Germany is clearly the pioneer in the field of national environmental labeling. Its "Blue Angel" program has been in existence since 1978 and is used by other countries as a model. Over 3,000 products in 57 product categories now carry the Blue Angel label. The program defines clean products as those which:

"when compared with other products fulfilling the same function and when considered in their entirety, taking into account all aspects of environmental protection (including the economical use of raw materials), are as a whole characterized by a particularly high degree of environmental soundness without thereby significantly reducing their practical value and impairing their safety."

It is claimed that a cradle-to-grave approach is used in evaluating products for the label; however, it appears that, lacking any outstanding environmental impacts in other areas, differentiation of products in a given category is usually made on a single criterion. This criterion may be recycled content, reusability, or some other environmental concern.

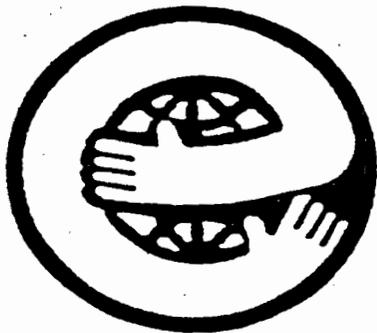
**Figure 1**  
**ENVIRONMENTAL LABELS USED**  
**IN OTHER COUNTRIES**



**WEST GERMANY - Blue Angel**



**CANADA - Environmental Choice**



**JAPAN - Ecomark**



**Nordic Environmental Label**

Criticisms of the program include: 1) failure to update (tighten) criteria; 2) not enough emphasis on quality and usability of labeled products; 3) use of a single environmental criterion; 4) failure to provide broader labeling opportunities; 5) no guarantee that an unlabeled product may not be equally as environmentally sound as a labeled one, or even superior; and 6) because of exclusion from consideration of some product categories, some manufacturers use their own labels, with resultant consumer confusion.

#### **CANADA: ENVIRONMENTAL CHOICE**

Canada's Environmental Choice program produced its first three guidelines in summer, 1989. As of October 1990, 26 product category guidelines had been submitted for public review or finalized and put into use.

The program literature discourages use of the term "environmentally friendly" in favor of referring to products which "reduce the burden on the environment." A product which is a good environmental choice is "any product which is made, used or disposed of in a way that causes significantly less harm to the environment than other similar products."

#### **JAPAN: ECOMARK**

Japan's environmental labeling program was launched in February 1989. The program aims to promote "clean" innovation by industry, heighten consumers' environmental awareness, recommend products which contribute to environmental protection and conservation, and symbolize an ecological lifestyle.

"Clean" products considered for labeling are those which cause little or no pollution when used or discarded, improve the environment in use, or otherwise contribute to conservation of the environment. The logo's use will also be applied to environmentally favorable activities such as recycling programs.

To qualify for the Ecomark, products must have been manufactured with attention given to preventive measures being taken against environmental pollution in manufacturing, product disposal not involving difficult processing, opportunity being available for conserving energy or resources through use of the product, demonstration of compliance with quality and safety laws, standards, and regulations, and price not being excessively higher than that of comparable products.

## **NORDIC COUNTRIES**

In November 1989 the Nordic Council of Ministers agreed to implement a voluntary environmental labeling program. Common criteria developed with the cooperation of all participating Nordic countries and a common label will be used. The environmental performance of selected product groups will be assessed in terms of such factors as raw material extraction involved, production processes used, and disposal methods available, and a set of minimum requirements will be established. In some cases, the label will be granted to the least harmful product in a group, while in other cases the label will be granted to products that represent an alternative, more environmentally sound means of satisfying consumer needs.

Participation of individual Nordic countries will be voluntary. Norway, Sweden, Iceland, and Finland have all indicated that they will participate, while Denmark is waiting to see whether the European Economic Community will adopt a labeling program before it decides whether to participate.

## **EUROPEAN COMMUNITY**

In 1989, a feasibility study on an EC environmental labeling system was conducted for the Commission of European Communities by the Danish Technological Institute in cooperation with the University of Lund, Sweden. The summary report was published in January 1990.

The EC has proposed a plan for an environmental labeling program in which companies apply to their national government for the label, which would be awarded by an independent jury set up at the EC level. Once established, the program would be taken over by the planned European Environmental Agency.

## **AUSTRALIA: GREEN SPOT**

Australia is preparing to launch a labeling program late in 1990. The Green Spot program is proposed to identify and label consumer products which are environmentally sound in terms of four broad impacts: 1) they cause substantially less pollution than other comparable products; 2) they are recycled and/or recyclable; 3) they make a significant contribution to saving non-renewable resources or minimizing use of renewable resources; and 4) they contribute to a reduction of adverse environmental health consequences. Types of products which are considered universally environmentally benign are not to be included in the labeling program.

## U.S. FEDERAL, STATE, AND REGIONAL ACTION

A task force of Attorneys General of eight states held a public forum on environmental marketing in March 1990. A report of the findings and recommendations, released in November 1990, calls on the Federal Trade Commission and the EPA to work jointly with the states to develop uniform national standards for environmental marketing claims. The EPA, FTC, and White House Office of Consumer Affairs have already begun meeting to address this issue. The Attorneys General task force, now representing ten states, will hold hearings on its environmental marketing recommendations in December.

Environmental labeling legislation has been introduced on the federal level, with Senator Frank Lautenberg's Environmental Claims Act of 1990. The Act calls on the EPA to provide uniform and accurate standards and definitions for environmental marketing claims.

In the absence of a nationally authorized environmental labeling program in the United States, individual states and regional organizations have begun to attack the issue of "environmental friendliness" and labeling. New York, Rhode Island, Connecticut, and New Hampshire have passed legislation governing use of a recycling logo, while California recently passed an Environmental Advertising Act. Legislative efforts primarily have been directed at defining and banning environmentally unacceptable goods, rather than promoting "clean" products. Judgments of whether or not goods are environmentally friendly are usually based on recyclability, degradability, and reusability.

Perhaps more than any other, the issue of degradability illustrates the differences in perceptions of what is better for the environment. While many states have bills seeking to ban nondegradable plastics, many bills have also been introduced to ban degradable plastics because of the lack of information on the identity and effect of products which may be mobilized by the breakdown of the material and the possibility of contamination of plastics recycling operations. Also, proposed legislation often does not specify a preferred or optimum substitute material for banned materials, or does not indicate that the environmental effects of substitute products have been thoroughly considered.

CONEG (Coalition of Northeastern Governors) has focused its attention on the issue of environmental responsibility in packaging. Its preferred packaging guidelines, in order of preference, are: no packaging, minimal packaging, consumable, returnable, refillable/reusable packaging, and recyclable packaging or recycled material in packaging. CONEG is also

supporting requirements for removal of toxic agents such as lead, cadmium, and mercury from packaging.

#### **LABELING ORGANIZATIONS**

Scientific Certification Systems of Sacramento, California, is one of the most recent entrants into the field of product certification and labeling, with its "Green Cross" program. The company certifies environmental claims in specific areas which can be scientifically documented and awards a seal to recognize products with outstanding achievements in these areas. As of September 1990, Green Cross had certified various products on the basis of recycled content, including products in the categories of paper products, glass containers, and recycled plastic bags. In the future Green Cross plans to look at products on the basis of biodegradability (soaps, detergents), energy savings (appliances), and production from sustainable, renewable resources. Eventually the organization may issue an overall environmental seal of approval.

Green Seal is another labeling organization with a different approach. Rather than focus on individual characteristics, Green Seal plans to evaluate products' environmental impacts on a cradle-to-grave basis. Public comments have been solicited on recycled paper criteria, and the first seals are expected to be issued in early 1991.

#### **ENVIRONMENTAL GROUPS**

The Pennsylvania Resources Council (PRC) sponsored an environmental shopping seminar in March of 1990. They also publish an environmental shopping guide, which recommends buying items packaged in recycled or recyclable materials or reusable containers and avoiding mixed material packaging and excessive packaging.

The New York Public Interest Research Group has put out a pamphlet which is similar to PRC's guide in its recommendations on packaging. Consumers are urged to avoid single-use, disposable items, difficult-to-recycle or non-recyclable packaging, and toxic packaging and to look for reduced, reused, and recycled products.

Among environmentalists, enthusiasm for green marketing is high. In an informal telephone survey, many environmental organizations were eager to hear of any developments in this area, particularly regarding the possibility of the beginning of a standardized approach to environmental labeling claims.

Many environmental shopping guides are now widely available, as well as "save the world" books that contain product/package recommendations. Shopping and environmental

action guides include books and pamphlets published by various individuals and environmental groups intended to provide the reader with information to use in making purchasing decisions, investments, etc., that will have the least effect on the environment. Most of these publications do not claim to provide the answer of what is environmentally best, but rather aim to help readers make informed choices or modify their habits in order to minimize waste and pollution and conserve resources. The following are only a few of the guides available: **Shopping for a Better World; The Green Consumer; The Green Consumer's Supermarket Shopping Guide; 50 Simple Things You Can Do To Save the Earth; How to Make the World a Better Place; and Save Our Planet—750 Everyday Ways You Can Help Clean Up the Earth.**

These guides generally appear to use a single-criterion approach to evaluating products. None attempted even a simplified life cycle assessment. When more than a single criterion is used, the presentation of data is often one-sided. Data on a single topic may vary considerably from book to book depending on its source.

#### **PRIVATE ORGANIZATIONS (COMPANIES, SUPERMARKETS, ETC.)**

Many manufacturers are eager to respond to environmental concerns by labeling their products "environmentally friendly." Many manufacturers are sponsoring evaluations of the environmental implications of their products. The results of these evaluations may be published in private reports, in informational pamphlets, or as advertisements.

Manufacturers' environmental labels typically are based on a single environmental criterion, providing no clue as to whether any other environmental impacts were considered. Common criteria for labeling claims are those with high public interest or visibility, such as recycled content, degradability, and lack of CFCs in content or manufacture.

In the various programs discussed, criteria have been developed for various product groups, groups selected for one or more of the following reasons: 1) the product is a major constituent of the waste stream; 2) the product has a significant impact on the waste stream due to toxicity, etc.; 3) product use provides a substantial environmental benefit; 4) the product meets safety and quality requirements for normal use; 5) product requirement levels for the label are high to challenge industry to meet or exceed current levels of clean technology; 6) the product is easy to evaluate; 7) the product is commonly used; and 8) the product does not shift environmental impacts from one area only to create problems in another.

## **CRITERIA THAT HAVE BEEN USED TO EVALUATE PRODUCTS**

Criteria that have been used to evaluate products are discussed below. Most "clean products" recommendations are based on one or a few of these criteria rather than a total environmental impact evaluation.

### **RECYCLED CONTENT**

Recycled content is the most popular and widespread criterion used. It is a popular criterion because of wide recognition and support by consumers; however, different groups may use different definitions or requirements for recycled content.

### **RECYCLABILITY/REUSABILITY**

In the United States, recyclability and reusability are widely used as criteria in legislation although definitions may vary. For example, proposals in Massachusetts and Oregon to ban environmentally unacceptable packaging differed in their definitions of "recyclable." Obviously, standard definitions of terms would be a step in the right direction. In addition, proposed legislation is not specific on the materials or containers that are to replace those deemed unacceptable.

### **DEGRADABILITY**

Degradability is a popular and widely disputed criterion. It has been heavily used as an advertising point, but is currently being questioned or even denounced by many environmentalists. Many manufacturers and retailers focus on degradability as a positive characteristic; however, at least one "environmentally conscious" mail order company has temporarily withdrawn its biodegradable plastic bags for re-evaluation of their environmental effects. Some legislative proposals have called for bans on nondegradable plastics, while others have attempted to eliminate degradables.

### **HAZARDOUS/TOXIC MATERIAL CONTENT**

This criterion can be used as justification for the necessity of environmental labeling or can be used to disqualify products from eligibility for labeling.

### **WATER POLLUTION IMPACTS**

Water pollution has not been a major criterion although it is given specific attention in several environmental guides, particularly those having to do with phosphates and bleaches in detergents and biodegradability of various household products.

## **SOIL POLLUTION IMPACTS**

This is another criterion that is an integral part of a cradle-to-grave analysis, but is not a popular single criterion for labeling, except perhaps in the case of organically grown foods. Soil pollution is given some attention as an issue associated with the disposal of batteries and concern about the fecal wastes in disposable diapers. It is also being mentioned as a concern regarding degradable plastics due to lack of knowledge about the identity and effect of degradation products.

## **AIR POLLUTION IMPACTS**

The most popular air pollution issue in the past few years has been CFC content or "ozone friendliness," which has been covered by labeling programs, environmental shopping guidelines, and proposed legislation. Labeling programs and shopping guides generally focus on aerosol products, while legislation tends to focus on foam plastics. Air pollution effects are also used as a criterion when discussing disposal of products by incineration.

## **NOISE POLLUTION IMPACTS**

This criterion is little used in the United States; however, it has been used as the primary criterion in labeling certain West German products, e.g., lawn mowers, car mufflers.

## **PRODUCTION PROCESSES USED**

The draft Canadian guidelines for re-refined oil and recycled cellulose construction materials specified acceptable processes for oil demetallization and hydrotreating and for use of a dry process to produce recycled paper products. These specifications were removed from the final guidelines.

## **USES OF RESOURCES (INCLUDING ENERGY)**

This criterion can be subdivided into use of energy and use of resources. Unless energy usage is the primary evaluation criterion, it is hard to tell whether it has been addressed in assessing environmental impact. It is difficult, for example, to determine whether the increased energy usage for collection, transportation, cleaning, and distribution of reusable products, such as refillable glass bottles, has been considered by legislative bodies seeking to ban certain disposable products.

Product recommendations on the basis of resource conservation are most often directed at plastics as a user of

petroleum (considered a non-renewable resource) and paper as a user of wood (considered a renewable resource).

#### **OTHER CRITERIA**

Other criteria that have been used are: use of more benign products/processes, general requirement of safety/usability, amount or type of packaging, provision of information for the consumer, overall corporate reputation regarding social/environmental issues, effect on rainforest, longer lasting or repairable products, weight or volume contribution to landfills or waste streams, or disposal problems.

#### **METHODOLOGIES THAT HAVE BEEN USED TO EVALUATE PRODUCTS**

##### **PRODUCT LIFE CYCLE ASSESSMENT**

Environmental problems potentially can be alleviated by either direct or indirect means. A direct means would include bans of specific materials, processes, etc., or economic incentives or disincentives (such as grants or taxes) which have an immediate effect. Examples of indirect means include the banning of a product or the substitution of one product for another in order to correct some problem not as clearly linked to the product. For example, the global warming problem could be addressed by banning products whose manufacture generates large carbon dioxide emissions.

The worth of either a direct or an indirect approach can only be assessed by a life cycle assessment which examines the entire complex of operations associated with a product. The theory behind the use of product substitution or banning as a means for environmental benefit is that if the product is not purchased, then the manufacturing and processing will cease and, along with it, the environmental consequences will cease. However, the substitute product also produces environmental consequences that need to be evaluated. A narrow focus analysis can greatly err in assessing the actual impact of any action that affects purchasing habits.

In comparing a given product or a set of products on two or more environmental issues, even life cycle assessment may not be enough to give adequate guidance. The reason is that there are no weighting factors that tell how to compare environmental impacts, for example, of one pound of toxic heavy metal sludge to one gallon of water usage or consumption of one Btu of energy.

Up to this time, life cycle assessments have focused on performing an "inventory" (listing and quantification) of the materials and energy used and environmental releases (air,

water, solid waste) from all stages in the life of a product from raw material acquisition to ultimate disposal (Figure 2). However, a group of life cycle assessment experts at an August 1990 workshop in Vermont sponsored by The Society of Environmental Toxicology and Chemistry agreed that a more sophisticated approach is needed. In addition to the inventory of energy, materials, and releases, the associated environmental impacts should be analyzed (entering into the areas of risk and hazard assessment), and the changes needed to bring about environmental improvements should be analyzed as well. Methodology for this more comprehensive type of life cycle assessment is currently being developed for the EPA.

#### **MATRIX APPROACH (PASS/FAIL)**

While the life cycle assessment approach is the most comprehensive methodology, a more common approach is use of a matrix with "pass/fail" ratings. For example, a widely used consumer guide in England lists a variety of packaging materials with a series of environmental criteria (recyclable?, degradable?, etc.,) with yes/no answers and some comments.

#### **WEIGHTING SYSTEMS**

A problem with either the life cycle assessment approach or the matrix approach is that decisions as to which criteria are most important are left to the reader or consumer of the product. For example, two products (say aluminum cans and glass bottles) can be compared using a life cycle assessment. One product may "win" based on air pollution impacts and the other may "win" based on the amount of solid waste to be disposed. Which is more important?

#### **ISSUES/TECHNICAL PROBLEMS TO BE RESOLVED**

#### **SELECTION OF PRODUCTS TO BE EVALUATED**

Several of the criteria used in product selection are somewhat vague or controversial, such as selecting products that are a significant factor in the waste stream (the issue here is definition of the term, "significant"), selecting products that are simplest to do, or selecting products that do not contain hazardous components.

#### **COMPLETE LIFE CYCLE ASSESSMENT VERSUS EASIER, QUICKER METHODOLOGIES**

Decisions must also be made as to whether a complete life cycle assessment should be made as opposed to use of easier, quicker methodologies. The main concerns here are time and expense involved in analysis versus environmental benefit, and

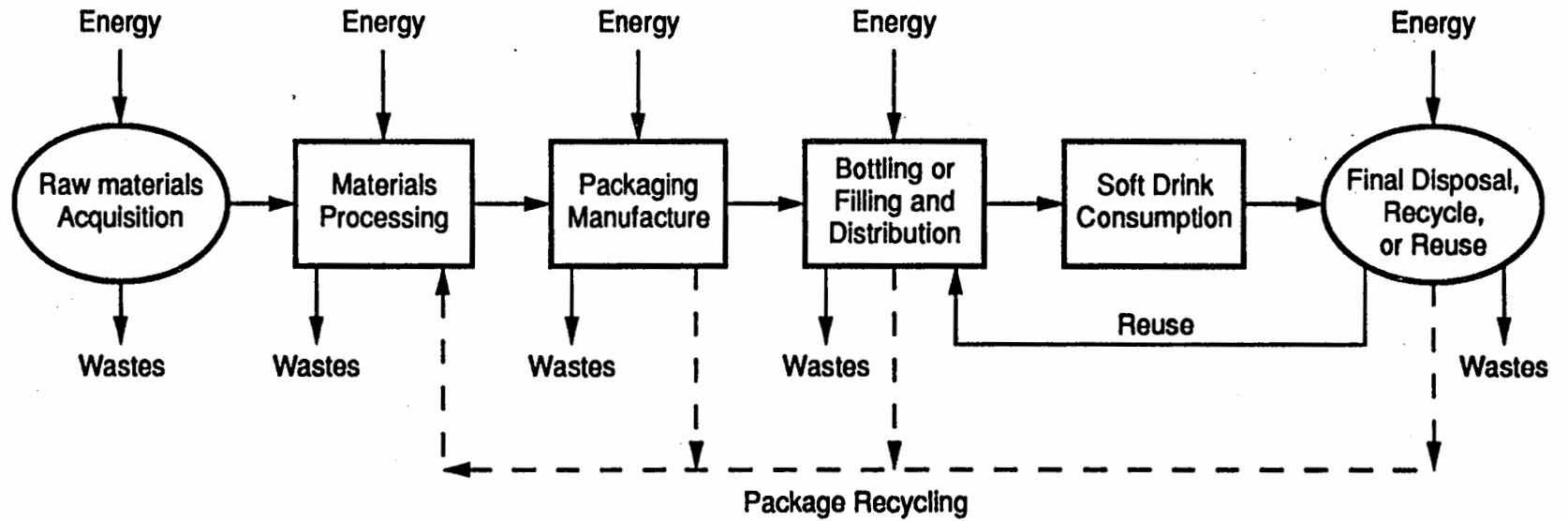


Figure 2. General materials flow for "cradle-to-grave" analysis of soft drink distribution system.

consumer loyalty and possible disillusionment or confusion. A true cradle-to-grave life cycle assessment is time-consuming, expensive, and raises difficult questions about weighting the relative importance of various environmental impacts. Also, once environmentally committed consumers have embraced an idea, it may be difficult to change their minds with the facts.

#### **HANDLING TRADE-OFFS**

In complete life cycle assessments, summaries of environmental impacts, such as total energy usage or water usage associated with one product, can be directly compared to the same impacts associated with another. Problems arise over weighting different impacts relative to each other. There are no established scientific methodologies for deciding which is more important. Some ways to handle these trade-offs are: weighting systems (this involves subjective judgment as to which components are least desirable or most harmful); pass/fail systems (using quantitative comparisons with minimum or maximum allowable levels); letting the consumer decide (abandon a simple logo and present environmental impact information, letting the consumer decide what is environmentally preferable); or using only one easily determined criterion (the advantage is easy evaluation by consumers, but the disadvantage is oversimplified and possibly erroneous conclusions on environmental impacts).

#### **IMPLEMENTATION ISSUES**

There are several options as to who should implement labeling programs. Some clean product programs are in effect at the national level, but not in the United States. A number of states, however, are moving in the direction of some kind of "environmentally friendly" product regulations. The states that are in CONEG have been particularly active in this regard. Environmentalist or other nonprofit groups also are involved in studying clean product/source reduction issues. Finally, many private companies have been carrying out their own initiatives, sometimes in connection with groups like CONEG.

#### **POLICY IMPLICATIONS**

There would be some advantages to implementing a clean product program nationwide. However, having a federal program would not necessarily preclude states or other organizations having their own programs as well. There would be the need to determine which agency(ies) would implement the program, research would be required, and an implementation mechanism would have to be developed and administered.

Another issue is the necessity to update the criteria used to measure products. These criteria can change with time as

research provides new information on environmental phenomena. Also, new products are continually being developed, and processes used to manufacture products also evolve over time.

## RECOMMENDATIONS

Both manufacturers and consumers generally appear to recognize the potential benefits of labeling. As yet, however, no universally accepted and supported course of action has been identified. Current efforts by various individual groups may be well-intentioned, but do not adequately address the comprehensive environmental impacts associated with a product's entire life cycle and, therefore, may offer consumers misguided direction.

Additional effort in several areas could aid in the development and support of clean products programs. These areas include: standardized definitions and usage of environmental impact terminology, survey of consumers to find out what types of information/education would be most useful, further development of methodologies to thoroughly and effectively evaluate products on a life cycle basis, development of a standardized environmental labeling program, and other reward incentives for manufacturers who provide cleaner products.

Additional measures that could minimize environmental impacts of consumer products might include: education on proper use and disposal of products, elimination of high environmental impact products for which acceptable, less damaging alternatives exist, elimination of excess packaging, and efforts to reshape today's convenience-oriented consumer perspective to a more environmentally responsible attitude.

The benefits to the environment, and consequently to mankind, that may be gained by support of clean products are considerable. The information provided and issues raised in this report can serve as a starting point.

INDUSTRIAL POLLUTION PREVENTION STRATEGY:  
RESEARCH PRIORITIES AND OPPORTUNITIES FOR THE 1990'S

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**ABSTRACT**

This paper is based on research performed under contract to EPA for the purpose of helping the Agency (Pollution Prevention Research Branch) establish a data base for use in identifying pollution prevention priority research areas. This research study determined what constitutes the more serious pollution problems within the industrial sector, what solutions have been tried, and what opportunities exist for technology transfer or basic research. The project was structured around the existing Standard Industrial Classification (SIC) system as a point of departure while also considering the information generated by the Toxics Release Inventory as reference. Direct knowledge and experience of people in specific industry and pollution prevention activities were also incorporated into the study.

On this basis, a resulting list of 17 high priority industries were identified, and for each, a more detailed assessment was performed to define major problems and pollution prevention opportunities.

The paper also discusses other developments that come into play as part in defining the course of research in this area such as the recent announcement by the Agency to pursue goals for serious reductions in 17 High Priority Contaminants. A list of recommendations is offered for improving project selection as well as future research prioritization.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

The 1984 Amendments to RCRA, the Hazardous and Solid Waste Amendments (HSWA), specifically mandates waste minimization as an objective for the nation's environmental management program (1). A means of implementing this directive has been the encouragement of source reduction and recycling approaches by both industry and the public. During the intervening years this policy has evolved into the Pollution Prevention Program that includes all waste generated, energy consumed and resulting relative risk to the environment and impact on ecological systems posed by human activity. The basic precepts of the program are the full understanding and voluntary cooperation of all parties (producing industry and consuming public) with regulatory incentives applied only when needed.

## OBJECTIVE

The objective of this research was to provide a data base that could be used as guidance by the EPA for the development of a research strategy for pollution prevention in the industrial area. More specifically, the objective was to identify a short list of industries, or industry segments, that present significant problems in terms of waste generated and/or opportunities for waste reduction through source reduction and recycling. Once identified, each of the industries or industry segments were to be studied in more detail to gather available information within that industry segment and to discuss the pollution prevention problems and opportunities with the various sets of personnel affiliated with each segment both in the public and private sectors, for the purpose of providing a basis for defining pollution prevention research projects.

## APPROACH

The study was designed to use the existing SIC system (2). A long list of SIC's (approximately 200) was to be developed along with a list of selection criteria (Table 1). The list is intentionally all inclusive and does not require the simultaneous satisfaction of all criteria.

This list was distributed to number of experts in the pollution prevention arena (state pollution prevention programs, various EPA departments involved with pollution prevention, the pollution prevention offices of the Regional EPA offices, other federal government departments, industry technical associations, and a small number of specific industry personnel). The participants were asked to review the long list of SIC's, and, in

the light of the selection criteria and their expertise, pick out 20 industries or industry segments and arrange them in priority order 1 through 20.

This, approach was largely dictated by the lack of readily available, good, quantitative data, defining the pollution hazard, the amount of pollution generated for each industry, beyond the Toxics-Release Inventory (TRI) reports (3) for hazardous waste, and the lack of rigorous definition of industries (SIC's or SIC segments) as they relate to pollution prevention.

TABLE 1. SELECTION CRITERIA FOR SIC's

- 
1. Importance of the industry to nation or society.
  2. Significance of all or certain waste streams in toxicity, volume or both.
  3. Large frequency of small and mid-sized firms that would benefit from government participation.
  4. Significant benefits that would be derived from waste minimization efforts that reduce toxicity and/or volume.
  5. Waste minimization is not expected to adversely impact product quality or marketability.
  6. Waste minimization would offer cost benefits, at least in long run.
  7. Waste minimization in this industry would be readily transferable to other industries.
  8. Industry has exhibited an interest in waste minimization.
  9. Waste minimization appears to be technologically achievable.
  10. Industry would benefit from government involvement because of lack of direction, capital, or technical sophistication.
  11. Industry would be receptive to waste minimization studies.
  12. The industry will not be viable in the long run without massive changes.
- 

This approach, has the potential weakness of leaving out a few priority areas while overstating others to a degree. This problem was not considered a serious flaw at this stage however, because the utilization of this information would only comprise one of the sources of data used for research planning by the EPA, with other

sources providing a system of checks and balances. This approach was taken as a starting point upon which further refinements would be made.

### IMPLEMENTATION

The development of the long list of SIC's, using informed judgement, resulted in a 175-item mixture of SIC industries and industry segments that were selected to generally fit the needs of the pollution prevention research criteria.

This list and the selection criteria of Table 1 were distributed among the organizations participating in the research prioritization, as discussed above, and the results compiled to define a short list of 17, high priority SIC's.

Once the short list of SIC's was determined, a significantly more detailed investigation was performed on each of the 17 by gathering available information, and discussions with the various experts in each field, technical associations, government and industry. For each of the 17 items on the short list, the results were compiled and also summarized in tabular format. Excerpts from these data are included under Results, below. The full project report and appendixes (4) are in process of being published as an EPA Project Report to be available from the National Technical Information Service in FY 91.

### RESULTS

The resulting short list of 17 industries is presented in Table 2. Presentation of the complete set of problems and opportunities is beyond the scope of this format. Sample results are discussed for two items on the list of 17 SIC's; #226-Textile Dyes Dyeing, and #753- Automotive Repair and Refinishing.

TABLE 2. SHORT LIST OF PRIORITY INDUSTRIES\*

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Textile Dyes and Dyeing.....	226
Wood Preserving.....	2491
Pulp and Paper.....	26
Printing.....	271-275
Chemical Industry.....	281
Plastics.....	2821
Pharmaceuticals.....	283
Paint Industry.....	285

Ink Manufacture.....	2893
Petroleum Industry.....	291
Steel Production Industry.....	331
Non-ferrous Metals.....	333-334
Metal Finishing (Electroplating).....	3471
Electronics/Semiconductors.....	3674
Automotive Manufacture/Assembly.....	371
Laundries/Dry Cleaning.....	721
Automobile Refinishing/Repair.....	753

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\* The list of 17 has been normalized (i.e., some of the industry segments have been aggregated in an attempt to present industry segments of equal pollution prevention significance. This list is in order of SIC number and not in order of priority.

The results presented per topic are far from exhaustive, due to business confidentiality and the limitations of the scope of this effort.

#### TEXTILE DYES AND DYEING (SIC-226)

Largely because of environmental concerns, the dye industry has undergone extensive change in the last few decades. Many of the dyes originally used (e.g., coal tar dyes, SIC 2865) are now considered toxic and have been replaced with material perceived to be less dangerous. New classes of fiber reactive dyes (e.g., triazine based) can reduce the use of azo dyes and contribute to lower concentrations of dyes during washing and rinsing. However, due to business confidentiality, specific technical information was not made available for this study (as was the case with several other industries).

In the textile dyeing and finishing industry, extensive changes have also been occurring, possibly as a result of changes in the fiber blends being produced. Chromates used for oxidation of vat dyes have been replaced by other chemicals; formaldehyde, used in dyeing and in durable press finishes, has been reduced or eliminated. The industry still requires a large amount of water and generates a large amount of wastewater. Progressively more automation is being introduced and this appears to contribute to better control and smaller releases of pollution to all media. This is still a developing area and improved process control software is needed to achieve further reductions.

Specific processes seem especially attractive for waste reduction opportunities. For example, wool scouring generates caustic wastewater. Processes such as hyperfiltration can be used

to recover the caustic from spent solutions for reuse/recycling. More cost/efficient membranes are needed to reduce the payback period and increase applicability.

Some dyes can be recovered and recycled. Economies of scale produce a significant barrier. The capital outlay to recover various types of dyes used are beyond present economics for other than large mills. Less expensive, smaller scale equipment is needed to fit the requirements of smaller mills, or mills that use a large assortment of dye types.

Solvent finishing is an idea that was explored approximately 20 years ago, but has now largely fallen into disuse. With rising costs, and stricter regulatory requirements, this approach could be re-examined. For example, where degreasing of wool fabric with caustic is currently practiced, solvent degreasing, with liquid and vapor solvent recovery may provide an environmentally attractive alternative. Such a "reverse" approach has been used outside the US (Compendium, ENV/WP.2/5/Add.85). A close look has to be made at the total picture so that short range economics are not traded for longer range environmental costs.

#### AUTOMOBILE REPAIR SHOPS (SIC-753)

The auto repair industry is a significant source of waste. Primarily, it is a collection of small shops. As a consequence, there is little structured pollution prevention research or allocation of staff dedicated to pollution prevention.

The major pollutants generated by the industry are waste paints, VOCs from spray painting, and metal-bearing dusts from paint overspray, grinding and sanding of finishes, degreasing solvents (often chlorinated) and oils and other automotive fluids removed during repair and used batteries.

The current means of managing liquid wastes is usually by off-site disposal, with the hydrocarbons either recovered by distillation, used for their fuel value, or simply destroyed by incineration. Small scale, on-site distillation equipment that would allow reuse of solvents is available but has not achieved a significant degree of use, partly because of regulatory requirements and lack of significant economic incentives. A demonstration of such an application would help to prove the cost-effectiveness of recovery, and make operational data available to the industry. The dusts generated by sanding and grinding can be collected by existing and innovative equipment, but at this time there have been no uses found for these mixed materials that could be considered pollution prevention.

In the area of spray painting, the major source of VOC emissions by the industry, there currently is no cost-effective technology for the significant reduction of these wastes for small operations. The spray booths being installed to comply with OSHA and environmental regulations, while maintaining surface finish quality, address only particulates (overspray solids) but not VOCs. There is a need for small scale solvent vapor recovery for this and other industries. EPA assistance in stimulating research in this area could result in major pollution reductions, both in this and other, small industries.

In principle, and based on a number of studies, it can be concluded that the application equipment and techniques used for spray painting are highly inefficient in terms of waste produced per unit of product due to overspray, atomization of volatile constituents into the air and/or water and the additional wastes resulting from equipment clean up, soiled protective clothing, etc.

More sophisticated coating technologies are and have been investigated, and are in use for certain applications. However, technology such as electrostatic painting, dip coating, etc. that are now making inroads in the facilities of Original Equipment Manufacturers are not yet practical or even appropriate for the refinisher. Recently, a low pressure/high volume (LPHV) spray gun has been introduced which markedly improves transfer efficiency and thus reduces VOC and particulate emissions.

While still to be fully developed, there is a significant list of other coating technologies intended to replace solvents, such as high-solids paints, U-V Curables, Ultrasonic activated, hot melt, etc., that could be advanced by research leading to application. Additionally, a number of these technologies are process specific, potentially limiting their wide adoption.

A half-way approach, using high pressure carbon dioxide in place of a portion of the solvents in paint formulations could become available in a few years and would contribute to significant reductions in VOC emissions.

The recharging/repair of automotive air conditioners may be an opportunity to recover Freon. Equipment is now available for such recovery and some types are in use.

Similar technology may be applicable to Freon recovery from commercial and residential refrigeration and air conditioning equipment, including the foam insulation panels. It should be noted in both areas that leakage of the unit, with loss of the Freon to the atmosphere BEFORE the unit arrives at the repair facility, is common. Investigation of improvements for recovery may be worthwhile. The substitution of organic and inorganic blowing agents and vacuum panels for insulation are some of the other approaches that could be evaluated.

Waste oil recovery is widely practiced by the industry, with the recovered oil usually being burned in commercial boilers or incinerators. Reprocessing of oil has had an on/off history over the past several decades, largely due to regulatory impacts. Innovations in waste oil reprocessing could return more of this resource to the consumer network. Some research is being carried out (Alaska, California) to extend the useful life of hydrocarbon-based oils by monitoring of deterioration and high performance filtering. Synthetic motor oils are another approach but do not appear to have attracted widespread consumer or vehicle manufacturer attention at this time. Evaluation of the waste/pollution associated with this product could be of interest.

Systems comparable to Freon or oil do not exist for waste antifreeze reuse and the bulk of this material probably ends up in POTWs or in mixed solvent wastes destined for incineration or fuel blending. The recovery and recycling of ethylene glycol contaminated with metals and chlorinated hydrocarbons (from solder and gasoline), plus other trace elements, needs additional research. Processes are available to remove solids by filtration, and additive (anti-rust) packages are available for reformulation or reconstitution. The present problem seems to be the development of a method/procedure for collection from small generators. The incentives that would make gas stations, repair shops and private residences participate in the activity in a much greater way do not seem to be present. An area of interest for research could be the characterization of the amount of antifreeze material discarded annually, its contaminants, the current management methods and associated problems. The resulting information would form the basis for design and decision-making regarding hardware and operating requirements for antifreeze recovery.

Batteries are another major source of waste from the automotive repair industry. Collection and recovery of the lead from the plates and suspended mixture of lead oxides and lead sulfate is extensively practiced. However, reuse of the waste sulfuric acid is not. Investigations and discussions with representatives of battery manufacturers have indicated that under proper operating conditions spent acid drained from batteries can be filtered to remove iron and copper contamination and the acid then refortified and recycled for battery use. The suggested research here would be to identify the specific problems and look for improvements leading to better technologies and associated economics.

Degreasing of vehicle parts can be considered integral to any repair or maintenance operation. Chlorinated and non-chlorinated hydrocarbons traditionally have been used in such operations. Recycling is widely practiced, often through off-site, contracted, services. Aqueous cleaning and degreasing solutions have been proposed and are being considered by some segments of the industry. Other technologies, such as blasting with solid carbon dioxide has

been tried. Careful evaluation of such products and procedures may produce pollution prevention answers useful to this industry.

#### GENERIC TECHNOLOGY

Investigation of industries within the short list resulted in the identification of generic pollution prevention needs applicable to many industries. These came in the form of unsolicited suggestions offered by a significant number of experts in the various fields of industry. These were finalized into a list of 13 generic research needs (see Table 3).

As indicated by various industry spokesmen, a number of generic or "core" research areas were identified where pollution prevention advances are needed. These would be applicable across a large number of industries or industry segments. Because of the large potential for improvements, it is recommended that these research areas receive significant priority in formulating a research program.

TABLE 3. LIST OF 13 GENERIC TECHNOLOGY IMPROVEMENTS NEEDED

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- VOC Control(Recovery technology)
- CFC Substitutes
- Oil-Water separation
- Improved seals for pumps and valves
- Equipment modifications
- Improved operational testing (process baths, etc.)
- Small-scale recovery for recycling
- Inventory control techniques for Pollution Prev.
- Metal degreasing
- Acid recovery
- Boiler waste reduction
- Adsorption systems for regeneration and recovery
- Industrial process scrap metal waste reductions

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#### VOC Control

With the current emphasis on air quality, it is somewhat surprising that more is not being done to develop technology for chemical vapor recovery. Many governmental agencies and industries appear to be satisfied to destroy vapors by incineration processes, at best recovering energy from the degradation of valuable chemicals. It is suggested that a large effort would be beneficial toward developing recovery/reuse approaches for such solvents.

This would affect industries as diverse as printing, painting (furniture, auto finishing), baking, etc. Currently, systems are available based on condensation by chilling or carbon adsorption; however, such systems are costly and apparently do not give the removal achievable with incineration techniques. And, where mixed solvents are used in a process, recovery must be coupled with reformulation or separation to produce usable solvents. Consequently, industry often chooses the destructive approach to satisfy regulatory constraints.

### CFC Substitutes

The quest for substitutes for the ozone layer damaging chlorofluorocarbons is well underway and several companies are heavily committed to the development of suitable alternatives. EPA may have opportunities to evaluate specific alternatives under development for specific applications; some of these will be chemically similar chemicals but others could be completely dissimilar chemicals or alternate processing methods. Alternate technologies that do not require fluorocarbons (e.g., for air conditioners, degreasing, plastic foam) would achieve major source reductions.

### Oil-water Separation

Many industries generate waste oil that is contaminated with water, or, in many cases, the water is the predominant species. For many processes, the current oil/water separation techniques do not produce reusable separate constituents. In some cases this accounts for large volumes of wastewater being generated. While some of the wastewater is suitable for reuse/recycle, many companies are still perceiving it more cost-effective to treat and discharge or dispose of it. Research on oil-water separation, such as, for example, emulsion breaking by either physical or chemical means would be widely useful. Activities involving cutting and cooling fluids, fluids such as those in metalworking or machining, petroleum refining and drilling are some of the sources of waste that could be reduced by research leading to improvements.

### Improved Seals for Valves, Pumps, etc.

A large plant has numerous valves which may be leaking at any one time. Improving the design or the seal material could conserve the materials being lost both as vapor and as liquid while minimizing the discharge to surface runoff, the air, or to wastewater collection systems.

Significant waste may be generated during start-up and shut-down of processes, both routine and unanticipated. Some of these discontinuities in operation are a result of premature failure of valves, seals, etc. Thus, improvements in longevity or predictability of seal failures could reduce waste such as spills, off-spec products, waste reagents or any feed and product material of a process. For example, the start-up of a printing press produces considerable waste paper as colors and registration are adjusted; the industry is now devoted considerable effort toward developing automated equipment that will minimize such start-up losses and allow change-overs "on the fly."

### Equipment Modifications

In a wide range of industries the same equipment is used today as has been used for decades. Significant processes are operated because they were "always operated that way." While it is difficult to identify specific industries or processes with a quick review, the potential for improvements after a focused study is significant. Resulting changes may lead to improved yields, decreased by-products, etc., and have a major impact on waste production. For example, a redesign of a reaction kettle or the use of a new design a baffle or stirrer could accelerate a desired reaction and/or improve yield. Even exhaust pipe sizing can affect the slight overpressure at which a reaction may be occurring. Incorporation of ultrasonic agitators or high pressure gas lances can improve the efficiency of reactions as well as the efficiency of reactor clean-out between batches, thus minimizing chemicals/solvents needed to achieve a desired level of cleanliness. While these types of improvements are, for the most part, practiced as routine improvements for reducing costs, increasing profits and staying competitive, the approach from a pollution prevention perspective (while keeping track of economics) offers new opportunities.

### Bath Testing (Manual Process Control, Small-Scale Operations)

Simple, convenient, quick tests are needed for operators to determine when a process bath, reaction mixture, or rinse water has reached its safe loading and thus help to determine when discharge is necessary. Certain of these tests do exist, but often they are not relied on by operators. Instead, discharges or disposal of baths, rinses, etc., are done on an arbitrary, routine schedule that may be exceeding required frequency and produce significantly larger volumes of waste. Recommendations are for feed-back and feed-forward control loops which allow optimization.

### Small Scale Recovery

Distillation, evaporation, carbon adsorption and regeneration, etc., while in common use, do not exist in widespread use at small scale for the purpose of recovering solvents from paints, degreasers and reaction vessels. Evaluation of hardware and economics on an impartial basis could provide needed information.

### Inventory Control

Automated inventory control has been shown to produce significant decreases in waste. Needed is software that is tailored to the small firm for tracking their raw feed materials, products and wastes generated. In addition to forming a convenient method by which to evaluate actual costs, it would also serve in placing focus on waste and liability costs and therefore create an environment for waste reduction incentives.

### Metal Degreasing

Vapor or liquid degreasers are widely used in industries ranging from semiconductors to auto refinishers. While considerable progress has been made in designing these to minimize solvent loss and carryover, indications are that solvent recovery still amounts to only about 60%. Total redesign of degreasers or consideration of many of the dragout control concepts used in the electroplating industry may be the necessary next step, as well as careful consideration of non-solvent alternatives such as aqueous or physical degreasing. Degreasing with aqueous solutions coupled with ultrasonics has received some attention for degreasing metal parts in Europe. Cleaning by blasting of various substances from sand to walnut shells has also been investigated. Another research area is to design processes that avoid needing the degreasing altogether.

### Acid Recovery

Recovery of strong acids (e.g., sulfuric, hydrofluoric, nitric, hydrochloric) has long been recognized as a desirable route to minimizing waste. However, capital cost for corrosion-resistant acid stills has usually limited their application to large centralized facilities - which then face the problems of transportation risks and costs. With the exception of hydrofluoric acid, recovery has not usually been cost-effective. An electro-dialytic bipolar membrane technology has been commercialized which allows recovery of concentrated acids and re-conversion of salt products to the acids (and bases) (Chem Eng., Dec 1989 p81). Such technology could have major impact on the steel industry;

chemical, dye, explosives, and other industries can also be investigated.

### Boiler Waste Reduction

Industrial power-generating boilers are a significant source of wastes, particularly during cleaning operations. California, in a summary of its 1988-1989 Waste Minimization Grants, noted that up to 11,000 tons of solid toxic waste is produced annually in that state from this source. While extensive research may be underway, the emphasis has not been on waste minimization. Reconsideration of this segment of industry with a source reduction viewpoint may elicit novel means of preventing the formation of water treatment sludges, etc.

### Adsorption Systems

Carbon adsorption is widely used for waste treatment and, less frequently, for chemical recovery. Other adsorbents have also been developed over the years (resins, zeolites, etc.). A research program examining cost and technical effectiveness of such different adsorbents - including regeneration - AND at developing chemical selectivity that might be achievable with one or more of these materials and that would allow systems to segregate waste components (from air, water, etc.) into reusable chemicals could be very productive. For example, water creates problems in carbon adsorption but certain hydrophobic zeolites do not readily adsorb water; consequently organics can be desorbed and recovered in an anhydrous state rather than as water/organic mixtures requiring further treatment. Newer, proprietary products with higher adsorption capacities are now being developed (Chem Eng Nov/89 p17). Support for development could be fruitful, particularly if applied to the recovery of more expensive solvents such as fluorocarbons, specialty esters, etc.

### Scrap Metals

A number of industries, including the finishing of castings, machinery fabrication, and auto refinishing, generate scrap metals as cuttings and turnings, grinding dusts, damaged parts, etc. These materials, often contaminated with cutting fluids, are usually discarded as solid waste or, at best, are sold to scrap dealers for reprocessing. Improved casting, forging, and machining processes and equipment would simultaneously reduce the waste loads produced and the amount of raw material used to fabricate the product. Such changes in production practices are usually brought about for reasons other than environmental concern, such as significant economics factors or regulatory pressures (e.g. worker safety). Where significant capital investment is involved, these

changes are very slow. Added stimulus could be productive via research that brings about a fore-runner or working example. The tool and die industry could be an area of focus.

#### RECOMMENDATIONS

Among a number of broadly-based needs recognized by this effort is the acute need for a classification tool, similar to the SIC used for this study. Instead of being based on a value of production/receipts/revenues basis (such as the SIC), it would be designed specifically for use as part of the pollution prevention work to serve as a means of comparing various data on a common ground. Approaches under consideration are concepts such as relative risk, true cost and life-cycle analysis. Some work has been started under these concepts but much effort is still needed before these can become practical working tools.

Within the industries investigated as part of this study, several appeared to lend themselves to EPA assistance for research more readily than others for the short range. In addition, there are many indications that rapid changes are, or will be taking place and that regular updating of this information should be scheduled to keep pace with developments, as well as to make improvements. The following recommendations emphasize those SIC's where it appears that EPA participation would be most productive. There is no priority indicated by position on the list.

- o Textiles - recovery of dyes and scouring agents from wastewater.
- o Wood preserving - investigations of new, less toxic preserving agents.
- o Pulp and paper - improved recovery of coated stock; restoration of fiber strength in recycled paper, deinking.
- o Printing - improvements in pre-press photographic chemistry through the use of computer technology; solvent recovery.
- o Chemical industry - substitution of less toxic solvents, solvent reuse/recycling. Process changes to eliminate use of toxic constituents.
- o Plastics - segregation of scrap plastics; compatibilization. Toxic solvent/cleaner substitution or reduction.
- o Pharmaceuticals - solvent reuse; substitution.
- o Painting - low and non-VOC painting techniques; improved application technology; substitution of less hazardous coating technology.

- o Ink manufacture - low and non-VOC inks; elimination of metallic pigments; substitution of less toxic inks, solvents and cleaners.
- o Petroleum exploration/refining - improved recovery of usable oil from drilling muds and processing wastewaters.
- o Steel industry - reuse of tar decanter sludge and electric arc furnace dust; reuse of recovered calcium fluoride.
- o Non-ferrous metals - isolation of arsenic contamination to allow reuse of stack dusts; improved hydrometallurgical processes minimizing sulfur oxide emissions.
- o Metal finishing - non-cyanide plating systems; improved chemical recovery from cyanide plating processes, toxic constituent substitution or reduction.
- o Electronics - "clean" fabrication techniques that eliminate or minimize degreasing solvent use. Mechanical cleaning technologies, reduction of toxic contaminants.
- o Automobile refinishing/repair - reductions in solvent losses in various operations, solvent substitution.
- o Laundries/dry cleaning - improved solvent recovery, process improvements.

This is the list recommended for priority pollution prevention research in the industrial area. Within each industrial segment considered a priority area, there are one or more suggestions, concepts, or problems. It is recommended that, with further refinement and updating, these can serve as one basis for the development of EPA research projects for the short term future.

Crossing the industries are basic, common needs that have potential for making significant pollution prevention impact. These were identified as the "generic" technology, above. These are a mixture of short-term improvements as well as longer-term, basic, or "core" research.

- o Improving chemical reaction rates or making reactions more product-specific, such as by improved catalysis, use of ultrasonics, use of microwave heating, improved reactor designs, etc.
- o Improved equipment/system reliability to reduce the need for start-ups and shut-downs that generate wastes.

- o Improved volatile organic chemical control, by development of equipment affordable by smaller companies to minimize losses from valves, pumps, etc. during use.
- o Material substitutions in product fabrication that avoid or minimize waste generation steps such as degreasing, electroplating and painting, etc.

Future refinements to the prioritization procedure should consider using a simplified list of criteria. A number of the expert participants stated that selecting candidate industries while keeping in mind a list of 12 criteria was counterproductive. Additionally, the Toxic Release Inventory (TRI) data and similar data available for providing amounts/toxicities/relative risk information should be incorporated into refinements as practical.

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THE EVALUATION OF AN ADVANCED REVERSE  
OSMOSIS SYSTEM AT THE SUNNYVALE, CALIFORNIA  
HEWLETT-PACKARD FACILITY

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ABSTRACT

The effectiveness of an Advanced Reverse Osmosis System (AROS) in the recovery of nickel plating bath solutions and rinse water was technically and economically evaluated at the Hewlett-Packard (HP) Facility in Sunnyvale, California under the California/EPA Waste Reduction Innovative Technology Evaluation (WRITE) Program.

The AROS is basically a reverse osmosis (RO) unit that provides zero discharge capability. This system has specially adapted membranes that do not require pH adjustments to neutral, a microprocessor control to manage the RO membranes, and a continuous monitoring system that monitors the influent, permeate, and concentrate for temperature, flow rate, and conductivity.

HP determined that the permeate and concentrate from the AROS unit could be recycled into the process; however, the payback period of 4.4 years was insufficient for capital purchase under HP's corporate purchasing policy.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

This study was performed under the California/EPA Waste Reduction Innovative Technology Evaluation (WRITE) Program, and was a cooperative effort between EPA's Risk Reduction Engineering Laboratory (RREL), the Alternative Technology Division of the Toxic Substances Control Program within the Department of Health Services (DHS) of the State of California, Hewlett-Packard (HP), and Water Technologies, Inc. (WTI). Science Applications International Corp. (SAIC) provided technical support on this WRITE project.

The WRITE Program is part of the RREL's pollution prevention research program. Under the WRITE Program, the cooperative efforts of the USEPA and state or local environmental programs are used to identify, develop, demonstrate and evaluate innovative pollution prevention techniques. Specifically, the WRITE Program provides engineering and economic evaluations plus information dissemination for methodologies that have the potential of reducing the quantity and/or toxicity of waste produced at the source of generation, or to achieve practicable on-site reuse through recycling.

In this project the effectiveness of an Advanced Reverse Osmosis System (AROS) in the recovery of nickel plating bath solution and rinse water was evaluated and the costs were compared with that of an existing chemical precipitation treatment system at the Hewlett-Packard Facility in Sunnyvale, California.

The plating operation that HP tested the AROS on was a nickel plating system consisting of two plating baths followed by a "dirty" rinse tank and then a "clean" rinse tank. The rinse water flows countercurrent to the flow of the items being plated. The overflow, 4 to 5 gpm, from the "dirty" rinse tank is a wastewater.

HP's existing wastewater treatment system for plating wastes (Figure 1) involves precipitation of metals as hydroxide salts. Chemical sludges are pumped to a recessed plate filter press system for dewatering. Dewatered sludge is disposed to an offsite disposal facility in California. Effluent from the precipitation tanks is pumped to ultrafilters for final polishing prior to discharge. Solids collected by the filters are then pumped to a filter press and then shipped and disposed offsite.

The AROS (Figure 2) is basically a reverse osmosis (RO) unit with specially adapted membranes that do not require pH adjustments to neutral. The unit includes a microprocessor control using proprietary software to manage the RO membranes. The unit contains a continuous monitoring system that monitors the influent, permeate, and concentrate for temperature, flow rate, and conductivity.

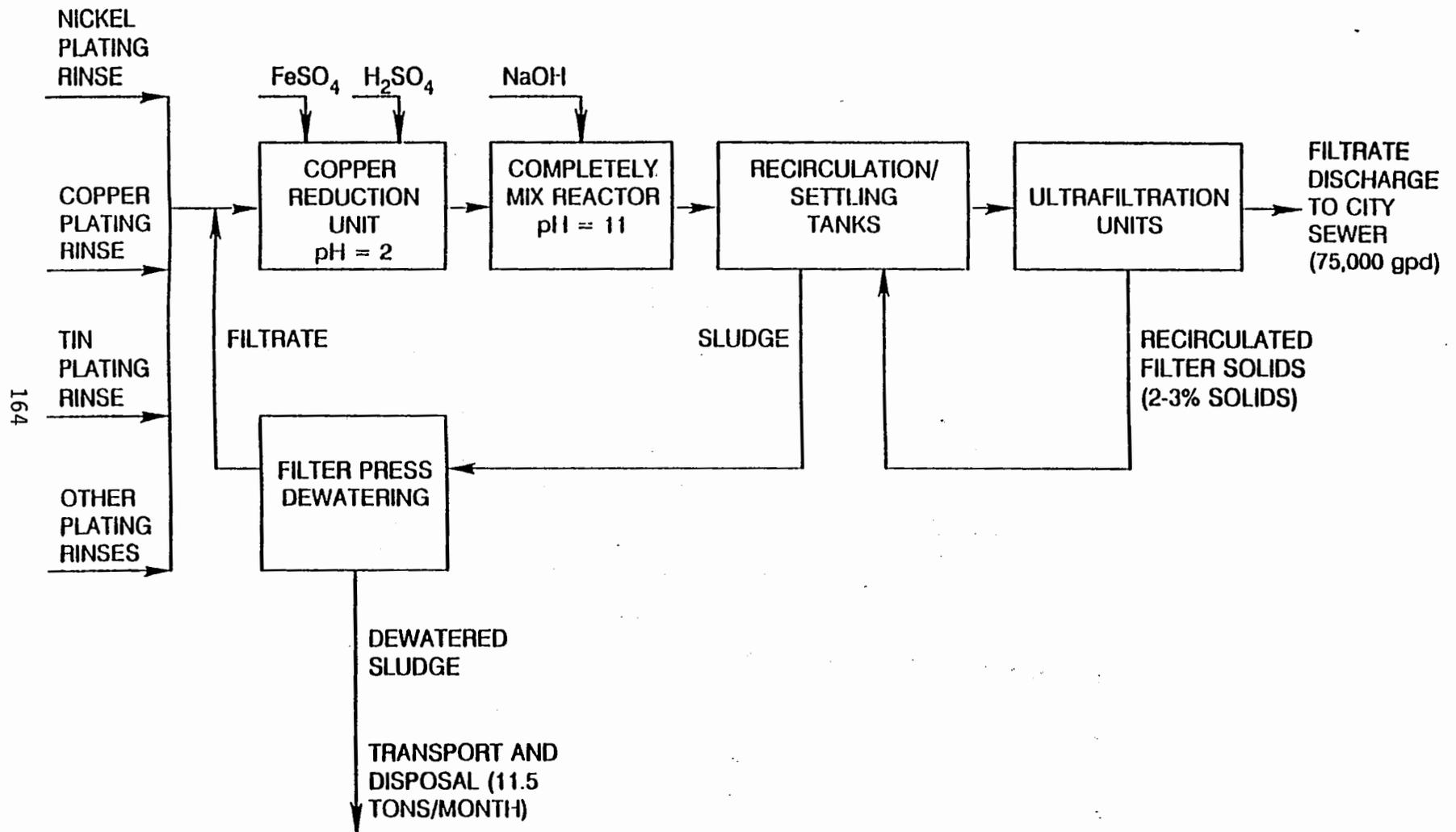


Figure 1. Schematic Diagram of Existing Wastewater Treatment System at Hewlett-Packard

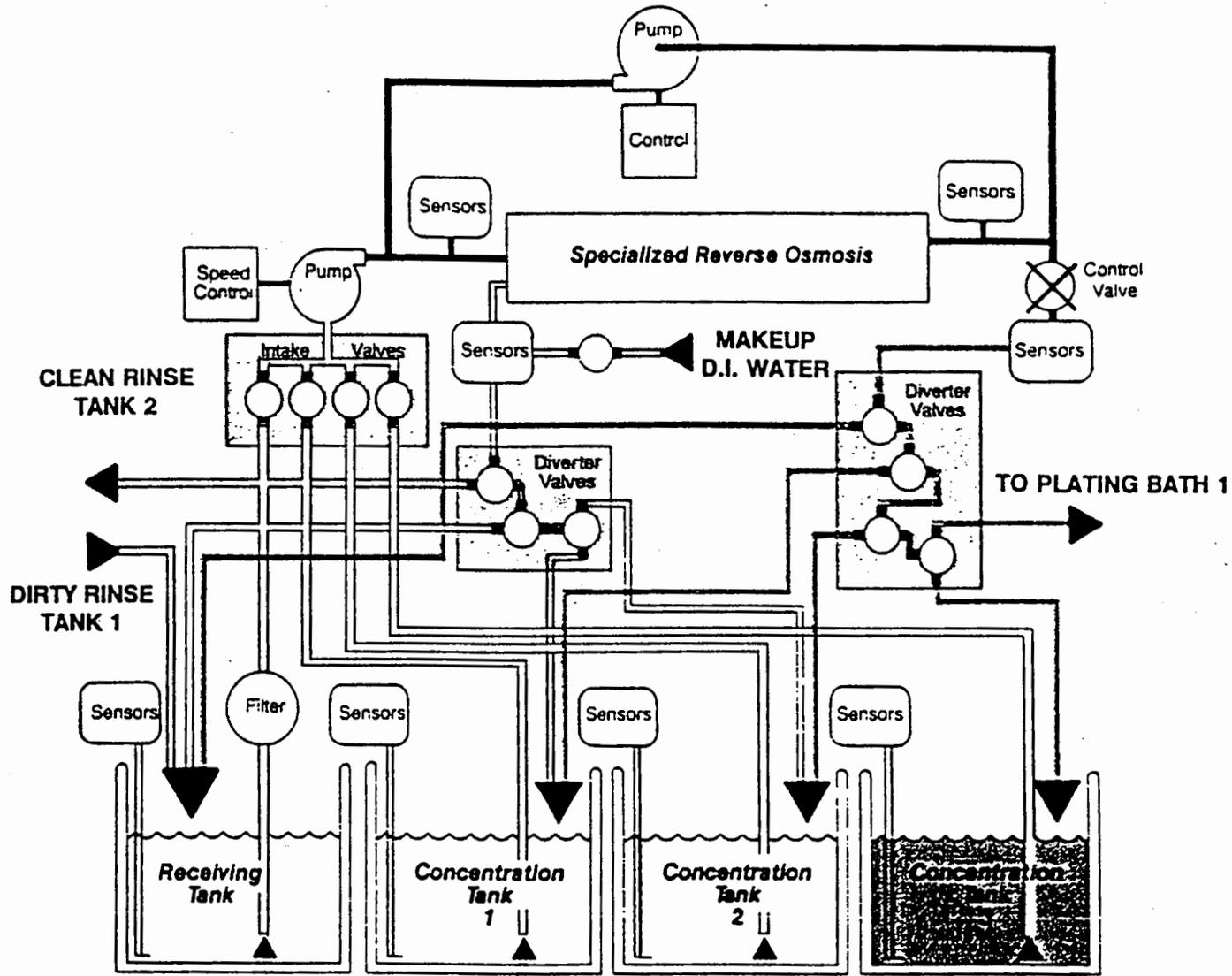


Figure 2. Diagram of the Advanced Reverse Osmosis System (AROS)

\* Courtesy of Water Technologies, Inc.

The RO membranes clean rinses to pre-specified standards and concentrate plating salts, in order to recycle both rinse water and plating salts. An AROS can reconcentrate dilute solutions to at or near bath strength (typically a concentration of 40% to 70 % is accomplished) without any evaporation or additional concentration technology.<sup>1</sup>

The AROS unit was installed at HP in November 1989. After initial installation and debugging, the system was test run from about November 21, 1989 to December 18, 1989. The system was temporarily taken off line at the end of 1989, to allow Hewlett-Packard to test and evaluate the plating bath quality and to create a baseline of comparison for bath contents and performance. Results were considered acceptable and the AROS unit was restarted in January 1990, and was operated on-line during most of 1990.

#### OBJECTIVES

This project includes additional sampling to establish a one-day snap shot of the AROS unit operation at the Sunnyvale facility. Removal efficiencies obtained based on the actual data were used to prepare a technical evaluation of the system. Economic analysis is based on data obtained from Hewlett-Packard. Details about the design of the sampling program are provided in the Quality Assurance Project Plan (QAPP).<sup>2</sup>

#### SAMPLING

Streams in and out of the AROS unit were sampled on October 17, 1990 to obtain a one day snap shot of the system's operation.

On Wednesday, 17 October 1990, SAIC observed sampling of the AROS unit installed at Hewlett-Packard in Sunnyvale. Hewlett-Packard staff conducted sampling while SAIC personnel supervised. The sample containers were prepared by Western Analytical Services Laboratory; labels were filled out and chain of custody maintained; and samples were placed in the bottles as explained in the QAPP. A representative from WTI, who manufactures the AROS unit, and Robert Ludwig of DHS were also present to observe sampling.

Four liquid streams were sampled as shown in Figure 3:

- 1) Influent to the AROS treatment unit which is the nickel plating rinse water from "dirty" rinse tank No. 1
- 2) Deionized water used as makeup water to the AROS unit
- 3) Permeate from the AROS unit which is clean water produced by the unit that is returned to the clean "rinse" tank No. 2

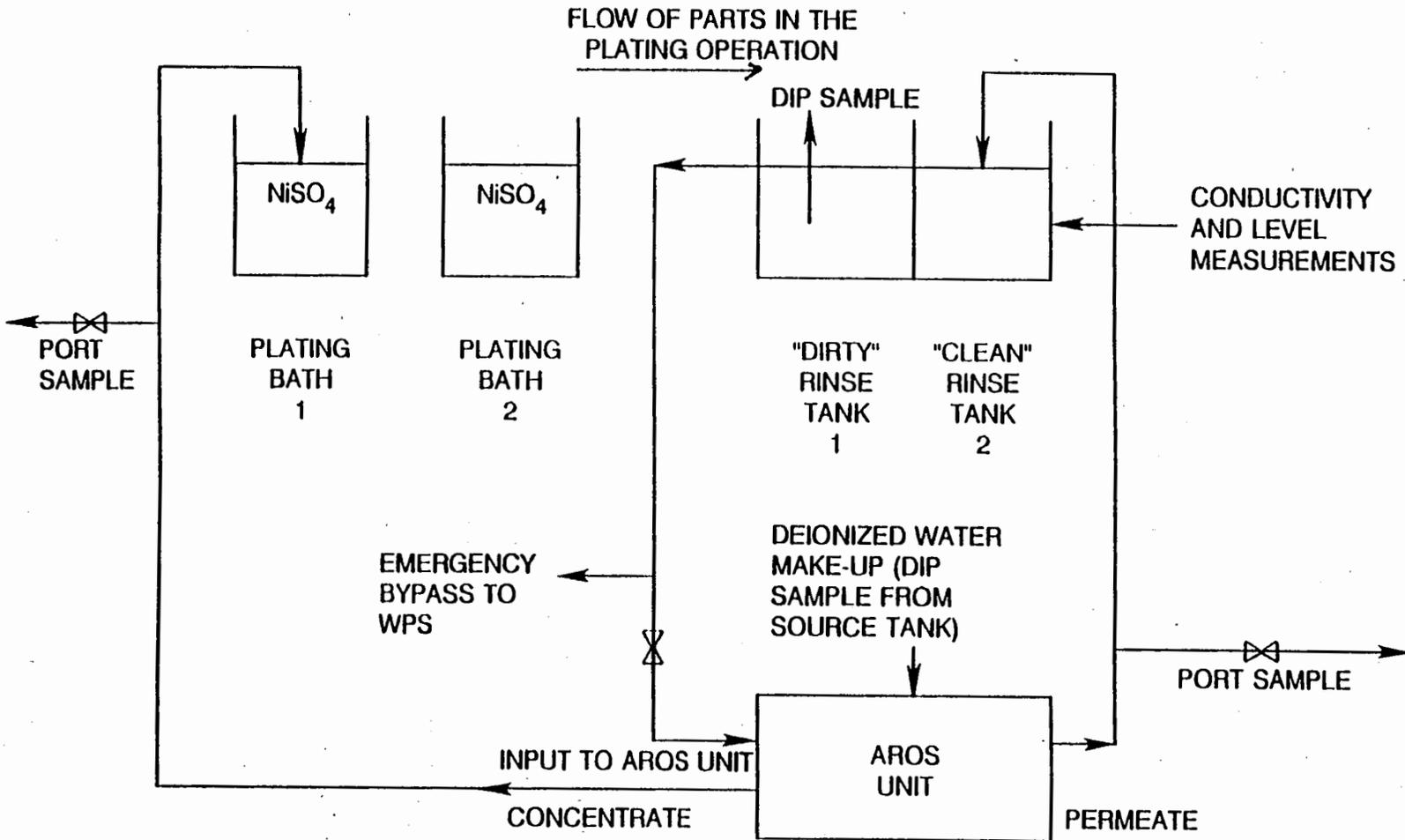


Figure 3. Schematic Diagram of the Advanced Reverse Osmosis System (AROS) for the Nickel Plating Operation and Sample Locations

- 4) Concentrate, consisting of approximately 50% nickel plating solution produced by the AROS unit and returned to the plating bath No. 1

Streams 1, 3, and 4 were collected as composites. Stream 2 was a one-time sample. Upon collection, all samples were stored on ice, with the exception of the concentrate, which would have crystallized if put on ice. At the end of the day, samples were poured into the prepared bottles for shipment to the laboratory. Samples from streams 1, 2, and 3 were shipped to the laboratory in a cooler with blue ice. The concentrate sample was shipped separately as a hazardous material and was not maintained on ice. The laboratory confirmed receipt of all samples in good condition the following morning at 10:00 am.

#### ANALYSIS OF SAMPLING RESULTS

Sample analysis includes nickel, chloride, sulfates, pH, total dissolved solids, conductivity, color, and total organic carbon. Sampling results are shown in Table 1. As can be seen in the table the AROS unit produced a composite permeate that was satisfactory as clean rinse water makeup, its intended purpose. Similarly, the concentrate was of quality (40% to 50% plating bath concentration) that could be used as nickel plating bath solution makeup.

#### ECONOMIC ANALYSIS OF THE AROS SYSTEM

The Hewlett-Packard Corp. (HP) maintains detailed cost records for their existing plating wastewater treatment system and deionized water production operations. These costs serve as a comparison for HP in their assessment of the cost effectiveness of the trial AROS unit. At HP the AROS unit only treated a small fraction, e.g. about 3 percent of the total plating wastewater flow.

At HP the savings from use of the AROS unit were directly related to the incremental reduction in spending for the following cost items:

Sewer discharge fees and water cost, estimated by HP at \$0.004/gal. or \$4 per 1000 gal.

Deionized water production cost, estimated by HP at \$0.0064/gal., or \$6.40 per 1000 gal.

Plating wastewater treatment costs, estimated by HP at \$0.0062/gal., or \$6.20 per 1000 gal.

Table 1. Sampling Results from Evaluation of the AROS Unit at Hewlett-Packard

CHEMICAL	UNIT	INFLUENT	CONCENTRATE	PERMEATE	DEIONIZED WATER	DETECTION LEVEL	PERCENT REMOVAL
Nickel	ppm	650	52700	20.5	0.19	0.01	96.8
Chloride	ppm	120	7800	29	ND	0.1	75.8
Sulfate	ppm	1100	79000	18	0.11	0.1	98.4
pH	—	6	4.1	5.65	6.1	—	—
TDS	ppm	2575	171500	165	ND	6	93.6
Conductivity	umhos/cm	1985	53750	139.5	3.75	0.5	93.0
TOC	ppm	30.8	1625	7.01	0.74	0.5	77.2

Note: In case of duplicate analysis results, arithmetic averages are used  
 Percent removal is calculated based on the  $((\text{Influent}-\text{permeate})/\text{Influent}) \times 100$  formula

It is understood that these plating wastewater treatment costs include:

- (a) Labor
- (b) Power
- (c) Chemicals
- (d) Expendable parts and supplies replacement
- (e) Monitoring, e.g. analysis of influent and effluents
- (f) Sludge treatment, transport and disposal

Purchase of new plating chemicals to make up for plating solution drag-out losses, estimated by HP at \$5.00/gal.

The above listed cost items are the major incremental cost savings resulting to HP from use of the AROS system as shown in Table 2, HP estimates the annual savings listed above to total \$26,250/year.

TABLE 2  
Estimated Annual Incremental Savings From Use  
of the AROS Unit as Reported by  
Hewlett-Packard Corporation, 1990 Costs

ITEM NO.	DESCRIPTION	ESTIMATED SAVINGS \$/GAL.	QUANTITY, GAL.	TOTAL ANNUAL SAVINGS
1	Sewer Discharge Fees and Water Costs	0.004	1,275,000	\$5100
2	Deionized Water Production Cost	0.0064	1,275,000	\$8160
3	Plating Wastewater Treatment Costs	0.0062	1,275,000	\$7905
4	Purchase of New Plating Chemicals at an 85 Percent Reduction	5.00	1260 x 0.85	\$5355

TOTAL ESTIMATED ANNUAL SAVINGS: \$26,520

This incremental cost savings is balanced against the annual expenditure for owning and operating the AROS system, as follows:

Electrical Power	\$1629
R.O. Membrane Replacement	\$2200
Labor and Expendable Parts	\$5000
Carbon Filters	\$ 90
Telephone Modem Contact With AROS Mfg.	<u>\$ 500</u>
TOTAL ANNUAL OPERATING COSTS	\$9419

Subtracting \$9,419/Yr. from \$26,250/yr., HP estimates that the net annual savings from use of the AROS unit would be approximately \$17,100/yr. The AROS unit costs approximately \$75,000, which represents approximately \$63,000 for the AROS unit plus another \$12,000 for making the installation permanent and training of operating personnel. The payback period is 4.4 years.

#### CONCLUSIONS

As shown in the economic analysis section of this paper, the Hewlett-Packard evaluation showed an estimated net annual savings of approximately \$17,000/year through use of the AROS unit. Under company policy this savings was insufficient to justify the capital expenditure of approximately \$75,000 (\$62,600 for the unit, plus installation and training costs). Hewlett-Packard has decided not to purchase the AROS unit.

Because the AROS unit treated such a small increment of the wastewater flow at HP it was difficult for the AROS unit to be cost effective; however, in a different setting the AROS unit might be very cost effective. Economy of scale worked against the AROS unit at HP. The purchase decision might have been different if the AROS unit been installed at a smaller facility where it would have treated a larger fraction, or even all, of the plating wastewater. Also, the AROS unit would be more economically competitive for a new facility that did not already have an amortized wastewater treatment facility in place.

The AROS unit performance was considered excellent.

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**THE BEHAVIOR OF TRACE METALS IN ROTARY KILN INCINERATION:  
RESULTS OF INCINERATION RESEARCH FACILITY STUDIES**

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**ABSTRACT**

Two series of pilot-scale tests evaluated the fate of trace metals fed to a rotary kiln incinerator. A venturi/packed-column scrubber was used in one series, and a single-stage ionizing wet scrubber was used in the other. Test variables were kiln and afterburner temperatures and feed chlorine content. Results show that bismuth and cadmium were relatively volatile, averaging less than 40 percent recovered in the kiln ash. In contrast, more than 75 percent of the arsenic, barium, chromium, copper, magnesium, and strontium were recovered in the kiln ash. Lead behaved as a volatile metal in one series, but as a nonvolatile metal in the other. Relative metal volatilities generally agreed with expectations based on vapor pressure/temperature relationships, although arsenic was much less volatile than predicted. Increased kiln temperature caused bismuth, cadmium, and lead to become more volatile, but did not affect the remaining metals. Increased chlorine content caused increased volatility of copper and lead. Metal fate was not affected by changes in afterburner temperature.

Increased kiln temperature caused the average flue gas particulate metal distributions to shift from roughly 20 to 60 percent less than 10  $\mu\text{m}$  for all test metals, except chromium. Metal enrichment correlated with relative metal volatilities, with the more volatile metals most affected. Increased chlorine content from 0 to 4 percent caused cadmium, copper, and lead distributions to shift from 20 to 55 percent less than 10  $\mu\text{m}$ . Increased chlorine to 8 percent had no further effect. For chromium, increased chlorine content from 0 to 4 to 8 percent caused a shift of 2 to 20 to 50 percent in particulate less than 10  $\mu\text{m}$ .

Average metal collection efficiencies for the venturi/packed-column scrubber ranged from 31 to 88 percent; the overall average for metals was 57 percent. For the single-stage ionizing wet scrubber, average metal collection efficiencies ranged from 22 to 71 percent; the overall average for metals was 43 percent.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

The hazardous waste incinerator performance standards, promulgated by EPA in January 1981, established direct particulate and HCl emission limits and mandated 99.99 percent destruction removal efficiency (DRE) for principal organic hazardous constituents (POHCs). These performance standards indirectly control emissions of hazardous constituent trace metals by limiting particulate emissions to 180 mg/dscm. Risk assessments conducted subsequent to the promulgation of the standards suggest that trace metal emissions from some incinerators treating waste streams with high levels of metals could pose unacceptable risks to human health and the environment. In response to this potential risk, the EPA has proposed regulations to establish limits on metal emissions from hazardous waste incinerators (1).

Despite the importance of metal emissions, there are only limited field data available to validate risk assessments and to assist regulatory development efforts. Data describing the effects of incinerator operation and waste composition on trace metal emissions are particularly lacking.

In response to these data needs, two series of tests were conducted at the U.S. EPA Incineration Research Facility (IRF) to determine the fate of trace metals fed to a rotary kiln incinerator. The primary difference between the two series was the primary air pollution control system (APCS) used for particulate and acid gas control. One test series was performed with a venturi/packed-column scrubber. The other test series was performed with a single-stage ionizing wet scrubber. The purpose of these test programs was to extend the data base on emissions and residual discharges of trace metals during incineration of hazardous wastes. Test data will support the EPA's Office of Solid Waste in its continuing development of regulations for hazardous waste incinerators. Test data will also be used to evaluate the predictive capabilities of a numerical metal partitioning model and to perhaps guide further model refinement (2).

The primary objective of these test programs was to determine the fate of five hazardous constituent and four nonhazardous constituent trace metals fed in a synthetic solid waste matrix to a rotary kiln incinerator. Of specific interest was the distribution of the metals as a function of incinerator operating temperatures and waste feed chlorine content. The five hazardous trace metals investigated were arsenic, barium, cadmium, chromium, and lead. The four nonhazardous trace metals investigated—bismuth, copper, magnesium, and strontium—were included primarily to supply data to support the model evaluation.

## TEST PROGRAM

All tests were conducted in the pilot-scale rotary kiln incinerator system at the IRF, illustrated in Figure 1. The main components of the system are the rotary kiln chamber, afterburner, flue gas quench, primary APCS, and secondary APCS. As shown, the quenched flue gas can be directed to either of the two primary APCSs installed in parallel. The flue gas is further treated by a secondary APCS consisting of a demister, carbon bed and HEPA filter before exiting to the atmosphere.

## SYNTHETIC WASTE MIXTURE

Similar synthetic waste feeds were used for both test series. The test waste contained a mixture of organic liquids added to a clay absorbent material. The trace metals were incorporated by

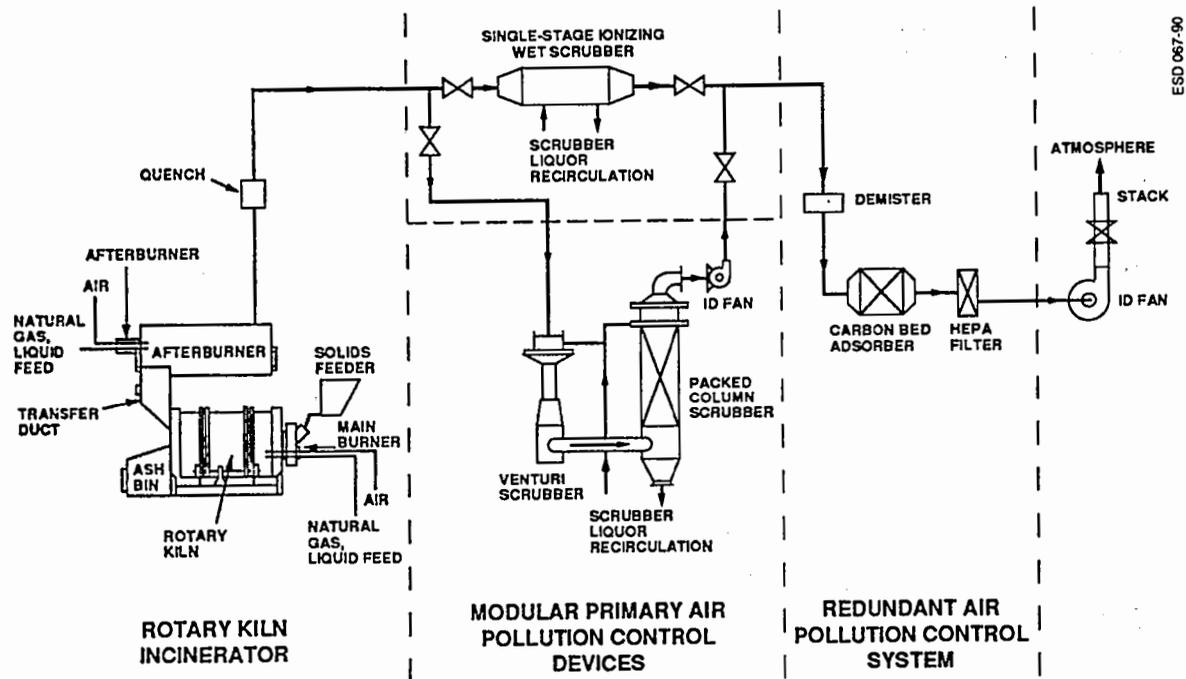


Figure 1. Schematic of the IRF rotary kiln incinerator system.

spiking an aqueous mixture of the metals onto the organic liquid-containing solid material. The resulting synthetic feed represented a solid hazardous waste containing both organics and metals. The waste material was continuously fed to the rotary kiln via a twin-auger screw feeder at a nominal rate of 63 kg/hr (140 lb/hr).

The organic liquid base consisted of toluene, with varying amounts of tetrachloroethylene and chlorobenzene added to provide a range of chlorine contents. Synthetic waste chlorine was varied from 0 to nominally 8 percent of the waste feed. The analyzed organic fractions for the three waste feed mixtures are given in Table 1. Table 2 summarizes the average metal concentrations in the combined waste feed.

### TEST CONDITIONS

The test matrix was the same for both test series. Table 3 summarizes the target and average achieved values for the three test variables. Each variable was varied over three levels, with the other variables held nominally constant. Target kiln exit temperatures were 816°, 871°, and 927°C (1500°, 1600°, and 1700°F). Target afterburner exit temperatures were 982°, 1093°, and 1204°C (1800°, 2000°, and 2200°F). Target concentrations for chlorine in the synthetic waste feed were 0, 4, and 8 percent. Both test series included replicate testing of one test condition to provide information on data variability. All tests were conducted under excess air conditions. Oxygen

**TABLE 1. ORGANIC COMPOUND CONCENTRATIONS IN THE SYNTHETIC WASTE**

Test series	Test	Weight % in mixture			Chlorine content*
		Toluene	Tetrachloroethylene	Chlorobenzene	
Venturi/ packed- column scrubber	1	23.2	0	0	0
	2 through 7 (average)	18.8	3.3	3.3	3.9
	8	14.6	7.1	6.9	8.3
Single-stage ionizing wet scrubber	1	23.1	0	0	0
	2 through 8 (average)	17.8	3.1	3.0	3.6
	9	11.6	6.0	5.6	6.9

\*Calculated based on measured tetrachloroethylene and chlorobenzene concentrations.

**TABLE 2. AVERAGE INTEGRATED FEED METAL CONCENTRATIONS**

Metal	Concentration (mg/kg)	
	Venturi/packed-column scrubber test series	Single-stage ionizing wet scrubber test series
Arsenic	44	48
Barium	53	390
Bismuth	150	330
Cadmium	8	10
Chromium	87	40
Copper	470	380
Lead	52	45
Magnesium	17,200	18,800
Strontium	280	410

**TABLE 3. TARGET AND AVERAGE ACHIEVED TEST CONDITIONS**

Test series	Test	Date	Feed mixture Cl content (%)		Kiln exit temperature °C (°F)		Afterburner exit temperature °C (°F)	
			Target	Actual	Target	Average	Target	Average
Venturi/ packed- column scrubber	1	9/14/88	0	0	871 (1600)	874 (1606)	1093 (2000)	1093 (1999)
	2	8/25/88	4	3.7	816 (1500)	825 (1517)	1093 (2000)	1071 (1959)
	3	9/16/88	4	4.2	927 (1700)	928 (1702)	1093 (2000)	1092 (1998)
	4	8/30/88	4	3.8	871 (1600)	878 (1612)	1093 (2000)	1088 (1991)
	5	9/7/88	4	3.6	871 (1600)	871 (1599)	1204 (2200)	1196 (2184)
	6	9/9/88	4	3.4	871 (1600)	875 (1607)	982 (1800)	983 (1803)
	7*	9/20/88	4	4.6	871 (1600)	873 (1603)	1093 (2000)	1094 (2000)
	8	9/22/88	8	8.3	871 (1600)	870 (1599)	1093 (2000)	1092 (1998)
Single- stage ionizing wet scrubber	1	8/17/89	0	0	871 (1600)	900 (1652)	1093 (2000)	1088 (1990)
	2	8/2/89	4	3.5	816 (1500)	819 (1507)	1093 (2000)	1095 (2002)
	3	8/4/89	4	3.5	927 (1700)	929 (1704)	1093 (2000)	1092 (1998)
	4	8/1/89	4	3.5	871 (1600)	877 (1610)	1093 (2000)	1096 (2006)
	5	8/16/89	4	3.7	871 (1600)	885 (1625)	1204 (2200)	1163 (2125)
	6	8/15/89	4	3.6	871 (1600)	887 (1629)	982 (1800)	1017 (1863)
	7†	8/9/89	4	3.6	871 (1600)	881 (1618)	1093 (2000)	1103 (2018)
	8†	8/11/89	4	3.8	871 (1600)	879 (1615)	1093 (2000)	1098 (2008)
	9	7/28/89	8	6.9	871 (1600)	881 (1617)	1093 (2000)	1087 (1988)

\*Test point 7 is a duplicate of test point 4.

†Test points 7 and 8 are replicates of test point 4.

concentrations were nominally 11.5 and 7.5 percent in the kiln and afterburner exit flue gas, respectively. Estimated solids residence time in the kiln was 1 hr.

### SAMPLING AND ANALYSIS

The sampling and analysis protocols were designed to track the discharges of the test metals in the incinerator residuals and flue gas. For each test, composite samples of the kiln ash and scrubber blowdown were collected. Flue gas sampling for metals at the scrubber exit was performed with a Method 5 train modified for metals capture (3). Samples of the clay and the aqueous metals spike solution were collected and the feedrates of each noted during each test. Kiln ash weights, scrubber blowdown, and scrubber liquor volumes were also determined for each test.

Flue gas particulate samples were collected at the afterburner exit during the single-stage ionizing wet scrubber test series. Using a variation of a Method 17 sampling train (4), at least 1 g of particulate was collected during each test. After obtaining the total particulate weight, these samples were size fractionated using a centrifugal classifier in accordance with the procedures in ASME Power Test Code 28 (5). The resulting size cuts were weighed, digested, and analyzed for metals.

Samples were digested following the procedures of Methods 3010 and 3050 (6). All metals analyses for the single-stage ionizing wet scrubber test series were by inductively coupled argon plasma (ICAP) spectroscopy per Method 6010 (6). For the venturi/packed-column scrubber test series, arsenic and lead analyses were by graphite furnace atomic absorption (6). Bismuth and strontium analyses were by flame atomic absorption (6). Analyses for the remaining metals were by ICAP.

## RESULTS AND DISCUSSION

### AVERAGE TRACE METAL DISCHARGE DISTRIBUTIONS

When subjected to incineration conditions, metals are expected to vaporize to varying degrees, depending on their relative volatilities. To characterize a metal's volatility, equilibrium analyses can be performed to identify the metal's volatility temperature for a given set of incinerator conditions. The volatility temperature is the temperature at which the effective vapor pressure of a metal is  $10^{-6}$  atm. The effective vapor pressure is the combined equilibrium vapor pressures of all species containing the metal. It reflects the quantity of metal that would vaporize under a given set of conditions. A vapor pressure of  $10^{-6}$  atm is selected because it represents a measurable amount of vaporization. The lower the volatility temperature, the more volatile the metal is expected to be. Volatility temperatures are a major parameter in the partitioning model used to predict metal behavior in an incinerator (2).

One objective of these tests was to identify the discharge distributions of the test metals relative to each other. To address this objective, metal discharge distributions have been summarized for each test program and presented in Figures 2 and 3. These figures show the amounts of metal found in each discharge stream normalized as a fraction of the total found in the three discharge streams—kiln ash, scrubber exit flue gas and scrubber liquor. In these figures, the bar for each metal represents the range in the fraction accounted for by each discharge stream over all tests of the respective test series. The average fraction for that test series is noted by the midrange tick mark. Metal discharge distribution data are plotted versus the metal volatility temperatures calculated assuming oxidizing conditions. For both test series, these figures indicate a correlation between observed volatility and volatility temperature for all the metals tested, except arsenic. With the exception of arsenic, the average normalized kiln ash fraction generally increased with increased volatility temperature.

Arsenic was much less volatile than expected, but behaved consistently for all tests. This observation is consistent with other studies at the IRF (7) and with studies at cement kilns (8). It is possible that arsenic forms a thermally stable compound in the incineration environment or becomes physically bound in the solid matrix.

Bismuth and cadmium were relatively volatile compared to the other test metals. On average, less than 40 percent of the bismuth and cadmium was recovered in the kiln ash, compared to an average of greater than 75 percent of the arsenic, barium, chromium, copper, magnesium, and strontium. Lead volatility behavior differed between the two test series. For the venturi/packed-column test series, the average fraction of lead recovered in the kiln ash was 20 percent. For the single-stage ionizing wet scrubber test series, the average fraction of lead recovered in the kiln ash was 82 percent.

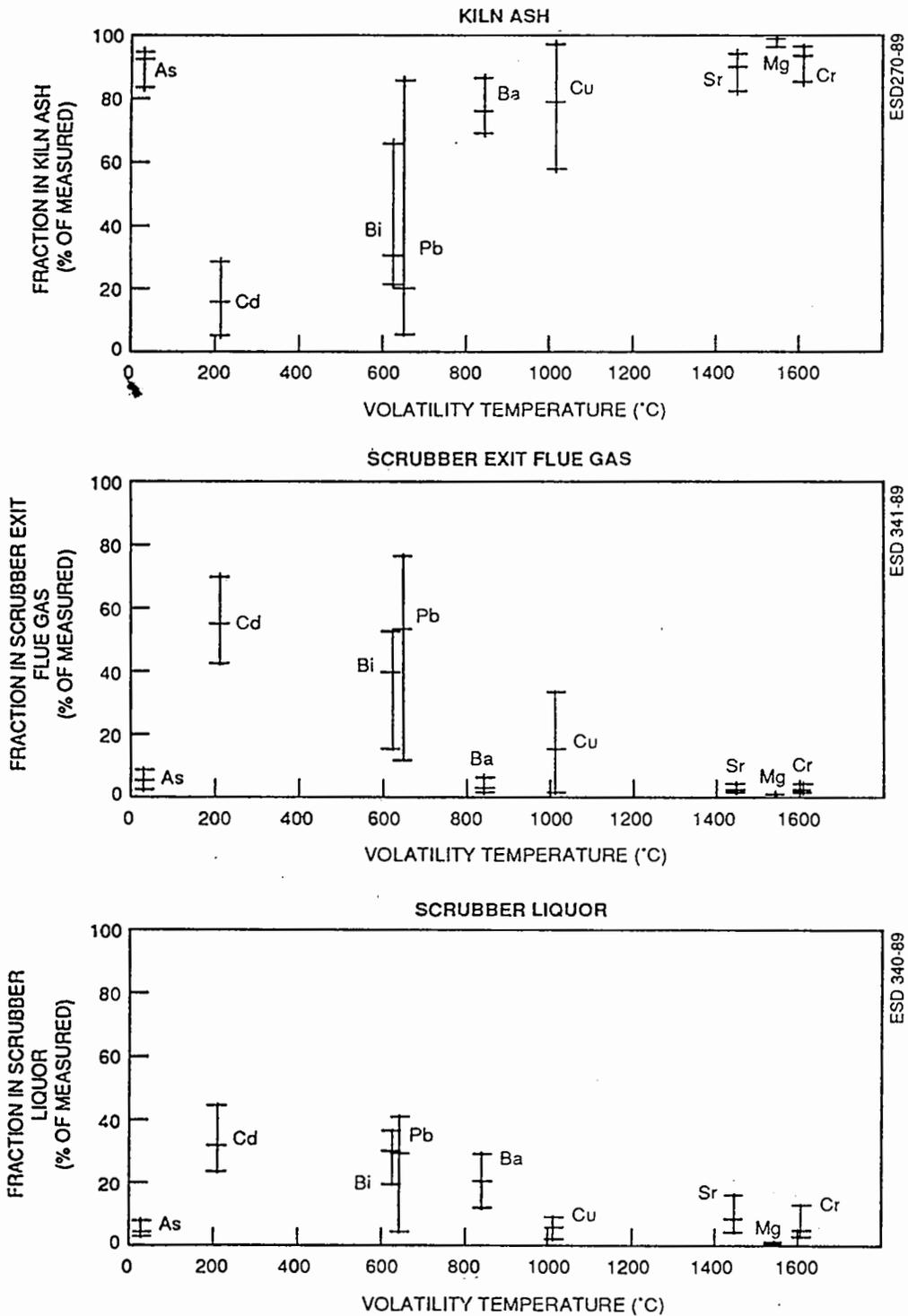


Figure 2. Distribution of metals in the RKS discharge streams in the venturi/packed-column scrubber tests.

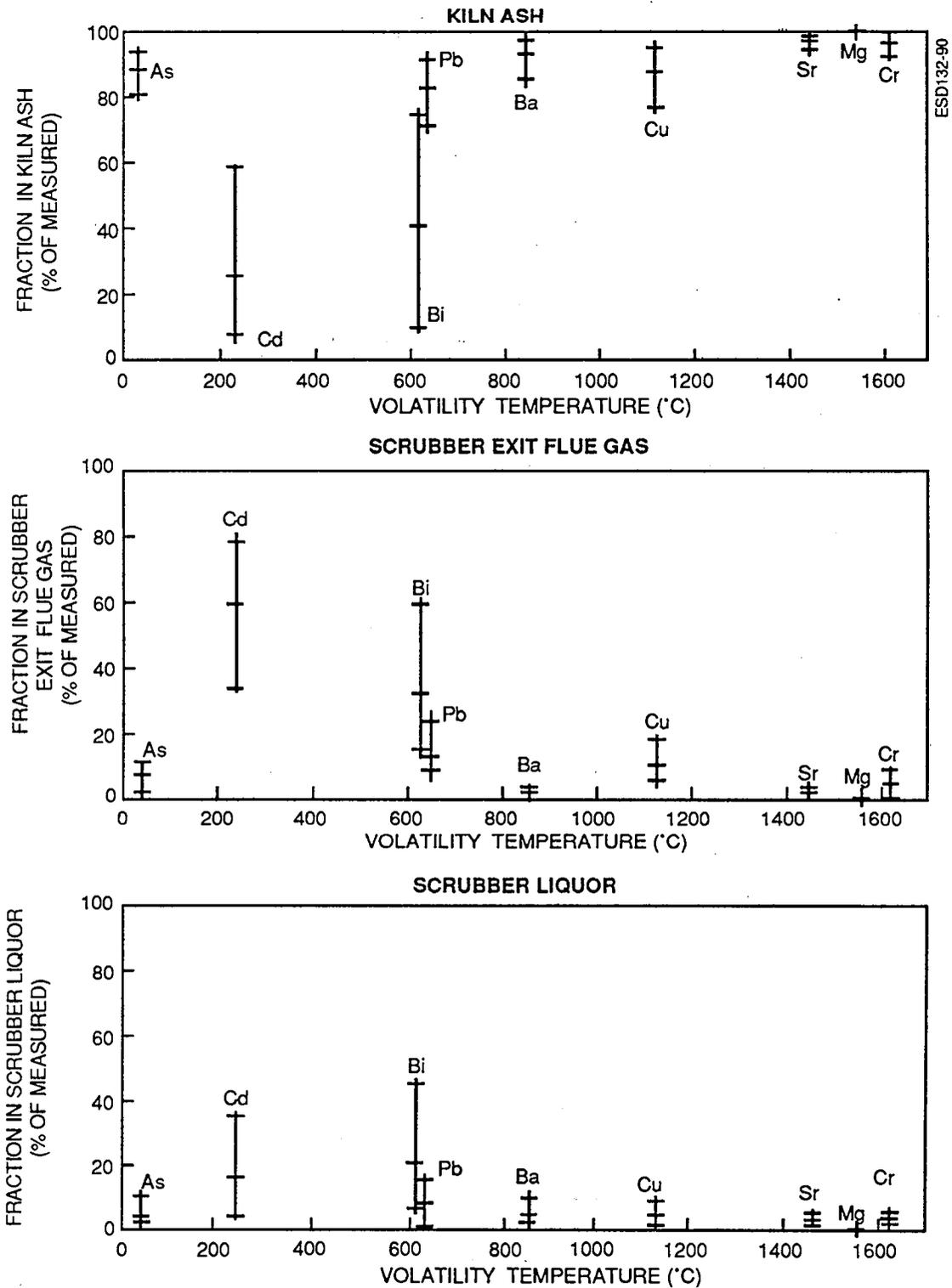


Figure 3. Distribution of metals in the RKS discharge streams in the single-stage ionizing wet scrubber tests.

The inconsistent behavior observed for lead may be because the volatility temperature of lead is within the range of kiln temperatures tested or may be related to increased lead volatility in the presence of chlorine. The volatilities of some metals may be altered through reactions in the incineration system. For example, chlorine can react with some metals to form new compounds that volatilize more readily. Many metal chlorides are more volatile, as indicated by a lower volatility temperature than their corresponding oxide or elemental forms. For example, equilibrium calculations for a mixture containing 5-percent chlorine result in  $\text{PbCl}_4$  as the principal vapor phase species. The corresponding volatility temperature of  $-15^\circ\text{C}$  ( $5^\circ\text{F}$ ) is considerably less than the volatility temperature of  $627^\circ\text{C}$  ( $1160^\circ\text{F}$ ) for lead under oxidizing conditions. Test data presented in the next section suggests that lead became more volatile with increasing kiln temperature and with increasing chlorine. Although the tests were performed under the same nominal conditions, minor differences between the two programs may have combined with the sensitivity to both of these test variables to cause the wide variation in lead discharge distributions.

## **EFFECTS OF INCINERATOR OPERATING CONDITIONS ON METAL DISTRIBUTIONS**

Test results from the single-stage ionizing wet scrubber test series show that increasing the kiln temperature from  $816^\circ$  to  $927^\circ\text{C}$  ( $1500^\circ$  to  $1700^\circ\text{F}$ ) caused a noticeable increase in the volatility of cadmium, bismuth, and lead. Figure 4 shows that as the kiln temperature increased there was a significant decrease in the kiln ash fraction of these metals, with corresponding increases in the scrubber exit flue gas and scrubber liquor fractions. Although the volatility of lead increased with higher kiln temperature, lead still remained relatively nonvolatile and was found primarily in the kiln ash for this test series. Changes in kiln temperature had no significant effect on the discharge distributions of any of the remaining metals. Data from the venturi/packed-column test series showed that kiln temperature had less pronounced effects on metal volatility.

Changes in afterburner temperature did not significantly affect the distributions of any of the metals among the scrubber exit flue gas and scrubber liquor discharge streams for either test series.

Variations in feed chlorine content did not affect metal discharge distributions within the limits of data variability established by replicate test conditions during the single-stage ionizing wet scrubber test series. However, as shown in Figure 5, increased feed chlorine content did cause increased volatility of copper and lead during the venturi/packed-column scrubber test series. As noted, the calculated lead volatility temperature is reduced significantly for cases that consider the presence of chlorine. The calculated volatility temperature for copper also decreases significantly when chlorine is considered (from  $1116^\circ$  to  $127^\circ\text{C}$  ( $1975^\circ$  to  $260^\circ\text{F}$ )). However, because neither metal was as volatile as would be expected if its volatility temperature were that of the metal chloride, it is suspected that only part of the lead and copper reacted with the chlorine to form the more volatile metal chloride species. The absence of a similar clear relationship between chlorine and the volatility of these metals during the single-stage ionizing wet scrubber test series also suggests that only partial reactions occurred.

## **METAL FLUE GAS PARTICLE SIZE DISTRIBUTIONS**

Metals find their way into flue gas particulate via two pathways. In one pathway, the metal remains in a condensed phase through the entire incinerator system and is carried out of the system with entrained ash in the combustion gas. In the second pathway, the metal vaporizes at some point in the incinerator, then recondenses when the flue gas cools. Both vaporization and condensation can occur locally under proper conditions.

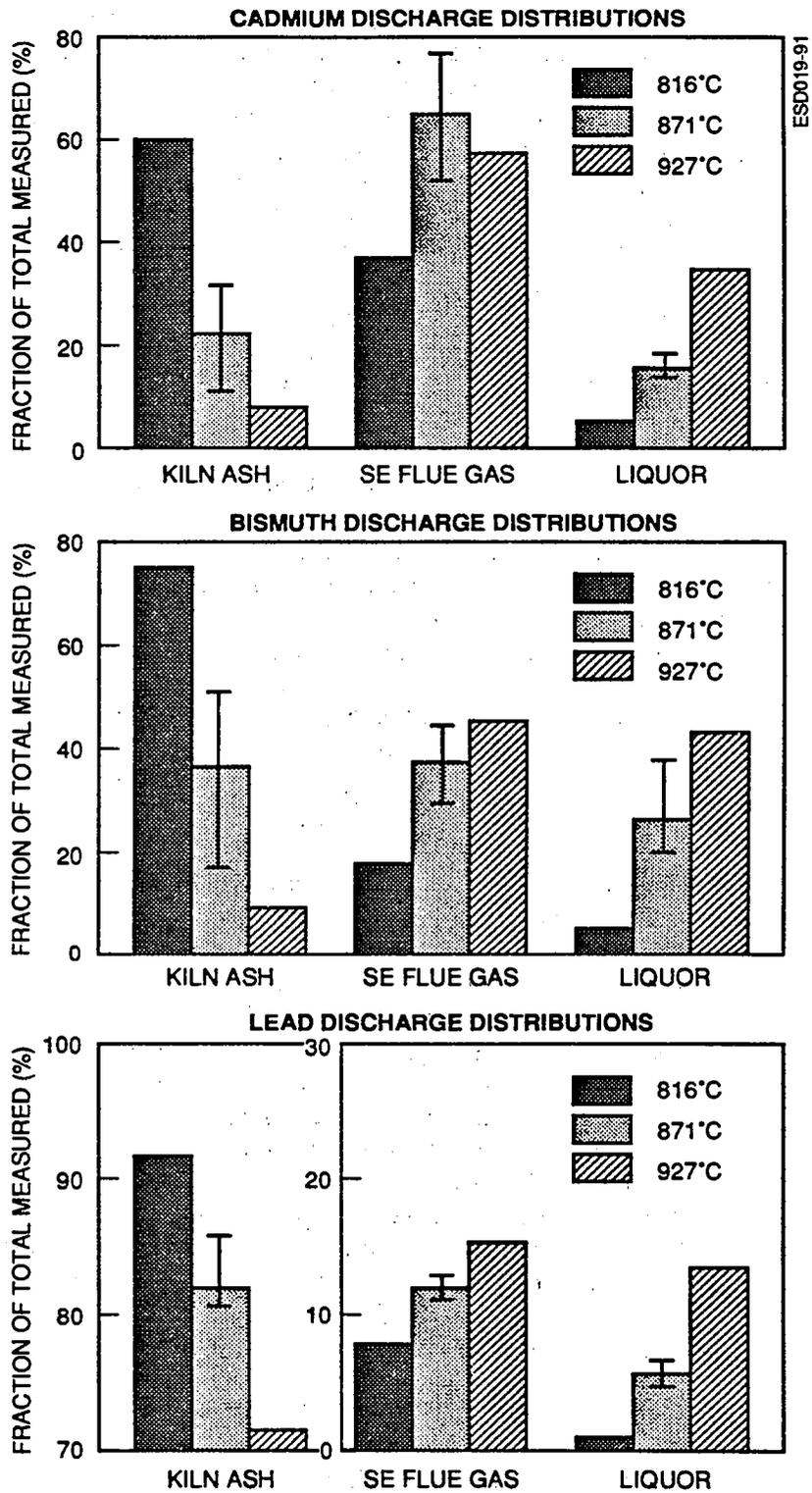
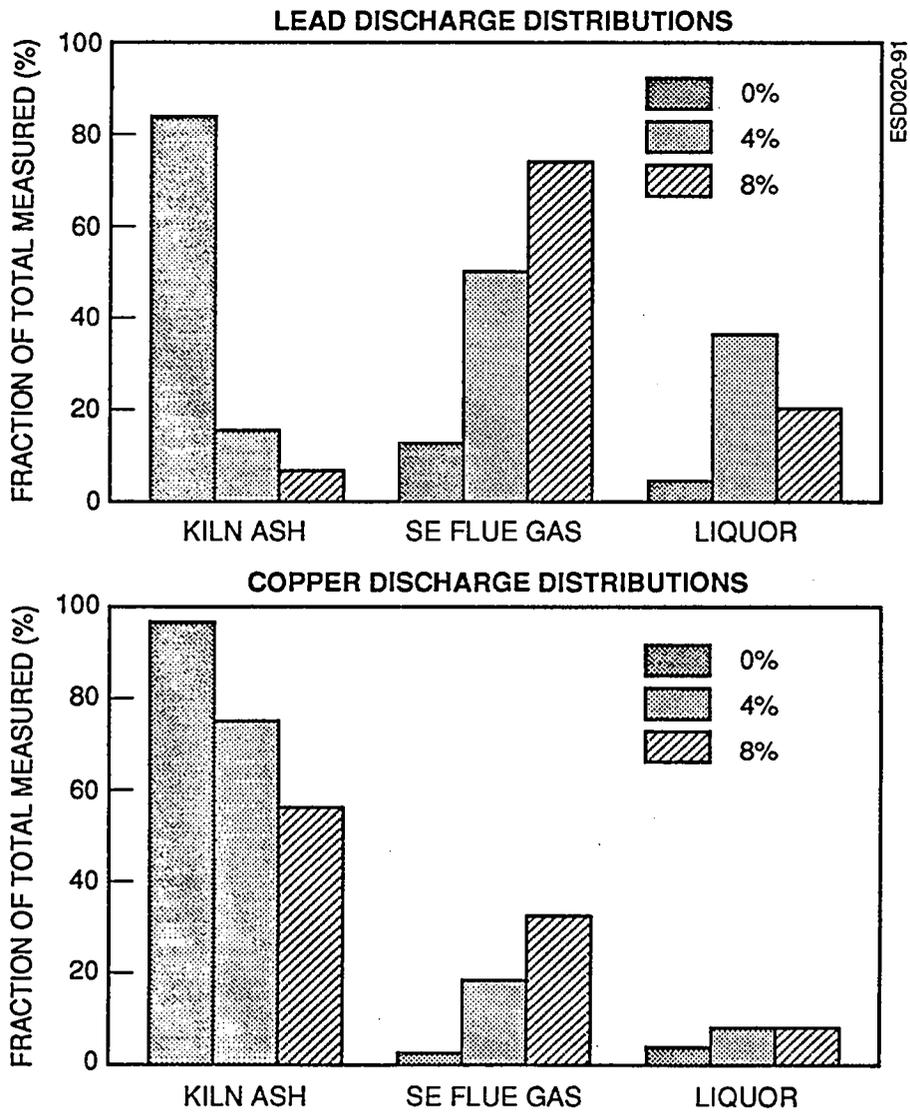


Figure 4. Effects of kiln temperature on the discharge distributions of cadmium, bismuth, and lead in the single-stage ionizing wet scrubber tests.



**Figure 5. Effects of feed chlorine content on the discharge distributions of copper and lead in the venturi/packed-column scrubber tests.**

Vaporized metals can condense homogeneously into condensation nuclei that grow into a very fine fume, or they can condense heterogeneously onto existing flue gas particulate. In both mechanisms the tendency is to enrich (be found at higher per mass concentration) in fine particulate. In the former mechanism, fume particles are very fine (1  $\mu\text{m}$  or less). In the latter mechanism, the surface-to-mass ratio is higher for fine particles than for coarse particles. Because condensation onto an available surface is a per surface area event, this also leads to enrichment in fine particulate.

Via the above mechanisms, the distribution of a given metal among flue gas particle size ranges is strongly influenced by the extent to which the metal vaporizes in the incineration system. Refractory metals that do not vaporize significantly tend to be relatively evenly distributed in the flue gas particulate size ranges on a per mass (mg/kg particulate) basis. Volatile metals tend to enrich in the fine particulate fractions, with enrichment tendency increasing with increasing volatility.

Figure 6 shows the fractions of the particulate metal found in the less than 10  $\mu\text{m}$  size range during the single-stage ionizing wet scrubber test series. The effects of increased kiln exit temperature are shown. The fractions of the total particulate sample in this size range are also shown. Values for the three replicate test conditions were averaged and plotted as a single point. Metal particulate distributions are plotted against the volatility temperatures to facilitate comparison of relative metal behavior.

With the exception of chromium, the average metal distributions in the flue gas particle size range less than 10  $\mu\text{m}$  shifted from roughly 20 percent to an average of 60 percent as the kiln temperature was increased from 816° to 927°C (1500° to 1700°F). In addition, the redistribution of metals to this size range generally correlated with the relative volatilities of the metals, with the volatile metals most affected. Interestingly, arsenic in the flue gas behaved as the most volatile metal with respect to particle size redistribution; more than 80 percent of the arsenic particulate was found in the less than 10  $\mu\text{m}$  size fraction at a kiln exit temperature of 927°C (1700°F). Although most of the arsenic remained in the kiln ash, the fraction that exited with the flue gas became significantly enriched in the fine particulate fractions during tests at higher temperatures. Observed enrichment of the test metals in the less than 10  $\mu\text{m}$  particulate suggests that some metal vaporization occurred in the system, even though many of these metals were predominantly nonvolatile as indicated by their tendency to remain predominantly in the kiln ash.

Although a relatively small fraction of the metal fed may escape the kiln, a propensity to concentrate in the finer particulate fractions may increase the risk posed by these emissions. These data are significant given the greater challenge to air pollution control devices posed by smaller particulate, the ability of smaller particles to penetrate the deep lung, and the toxicity of many metals. However, the data also suggest that metal enrichment in the fine particulate fractions can be controlled operationally by limiting incinerator temperature.

The effects of the waste feed chlorine content on total particulate and metal-specific size distributions are shown in Figure 7. When feed chlorine was increased from 0 to 4 percent, the fraction of total particulate in the less than 10  $\mu\text{m}$  fraction increased from 20 to approximately 35 percent. This is expected if the presence of chlorine in the feed serves to increase the volatility of some feed inorganic constituents. When reviewing the data, the effects of chlorine were taken to be most significant when the metal distributions were shifted more than the distributions of the

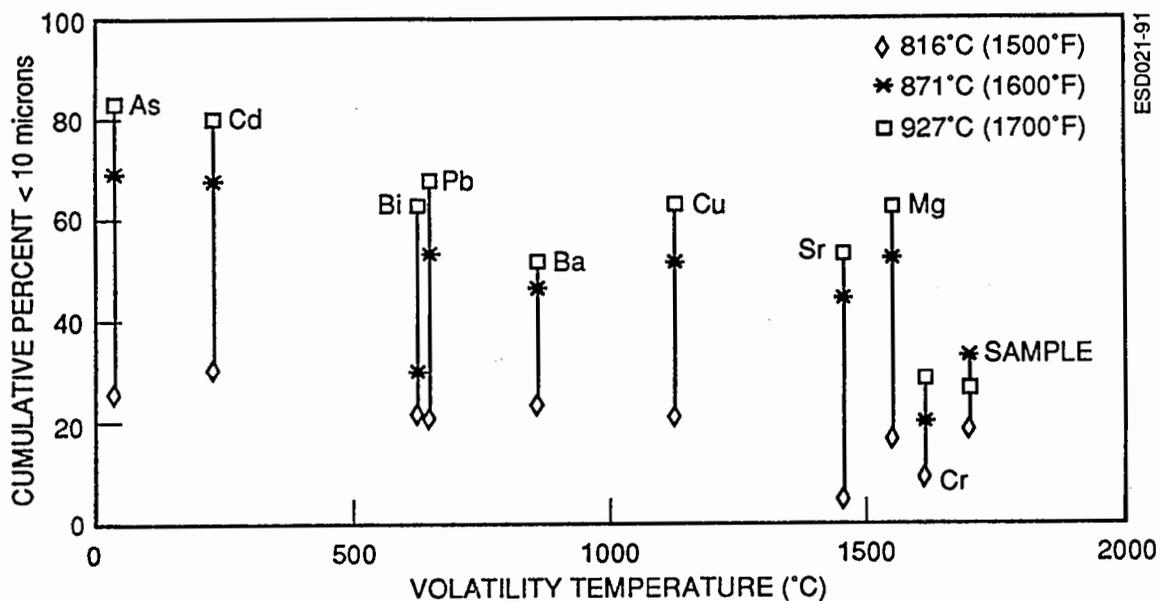


Figure 6. Effect of kiln temperature on the distribution of metals in the afterburner exit flue gas particulate size fractions in the single-stage ionizing wet scrubber tests.

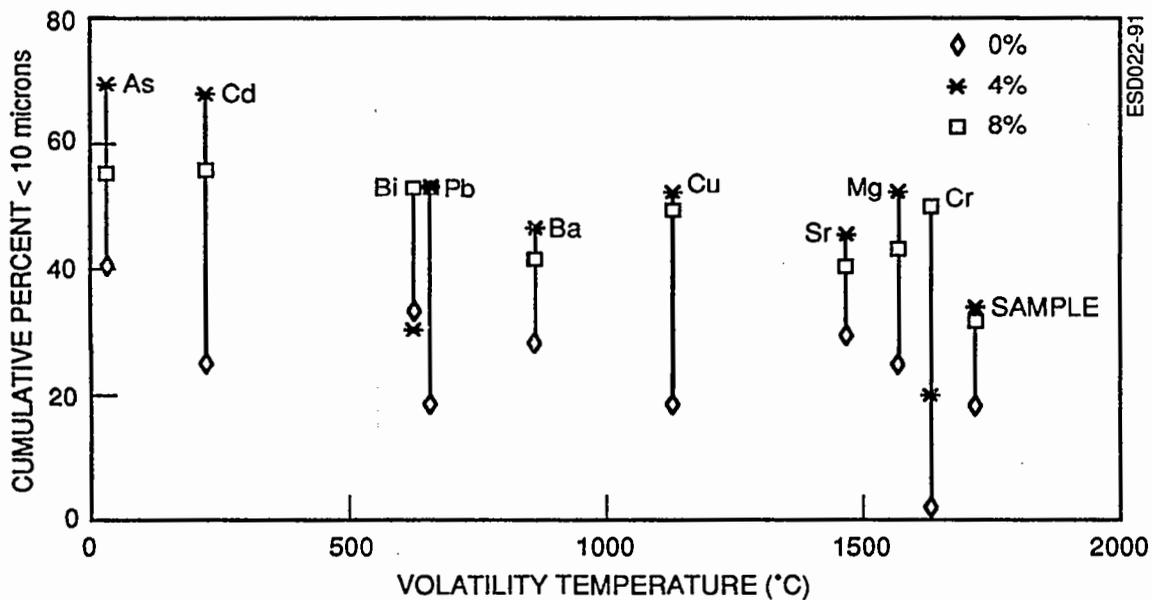


Figure 7. Effect of feed chlorine content on the distribution of metals in the afterburner exit flue gas particulate size fractions in the single-stage ionizing wet scrubber tests.

total particulate sample. Thus, flue gas particulate size distributions for barium and strontium and, to a lesser extent, arsenic, bismuth, and magnesium, were considered not to be significantly affected by waste feed chlorine concentrations. For these metals, the magnitude of the shift to the finer particulate fractions was about the same as the shift for the total particulate sample, primarily reflecting the shift in the particulate sample size distribution.

Chlorine had a more pronounced effect on the particulate size distributions of cadmium, chromium, copper, and lead. For cadmium, copper, and lead, the shift to finer particulate occurred with the initial feed chlorine content increase from 0 to 4 percent. The distribution of these metals in particulate of less than 10  $\mu\text{m}$  increased from approximately 20 to approximately 55 percent. No additional redistribution occurred with the further feed chlorine content increase to 8 percent. Chromium distribution in particulate of less than 10  $\mu\text{m}$  increased with both feed chlorine content increases, from 2 to 20 to 50 percent with chlorine increased from 0 to 4 to 8 percent. The impact on copper and lead particulate distributions is expected based on their reduced volatility temperatures in the presence of chlorine. Cadmium and chromium redistributions to finer particulate with increased chlorine are not similarly predicted by reduced volatility temperatures.

### APPARENT SCRUBBER COLLECTION EFFICIENCIES

The apparent scrubber efficiency for collecting flue gas metals was determined for each test. The apparent scrubber efficiency represents the ratio of the normalized metal fraction measured in the scrubber liquor to the sum of the normalized metal fractions measured in the scrubber liquor and scrubber exit flue gas. Figures 8 and 9 summarize the collection efficiencies for the venturi/packed-column scrubber and single-stage ionizing wet scrubber test series, respectively. The bar for each metal represents the range of scrubber efficiencies over the respective test series, with the average noted by the midrange tick mark.

For the venturi/packed-column scrubber test series, average metal-specific collection efficiencies ranged from 31 to 88 percent; the overall average for all metals was 57 percent. For the single-stage ionizing wet scrubber test series, average metal-specific collection efficiencies ranged from 22 to 71 percent; the overall average for all metals was 43 percent. Figures 8 and 9 show that the collection efficiencies for each metal varied significantly during each test series. However, average efficiencies were generally higher for the less volatile metals.

### CONCLUSIONS

The following conclusions are based on the results of the two completed trace metals test programs in the pilot-scale incinerator at the IRF:

- In the rotary kiln incinerator, cadmium and bismuth were relatively volatile. Over all tests, the average fractions of these metals recovered in the kiln ash was less than 40 percent.
- In the rotary kiln incinerator, arsenic, barium, chromium, copper, magnesium, and strontium were relatively nonvolatile. Over all tests, the average fractions of these metals recovered in the kiln ash was greater than 75 percent.

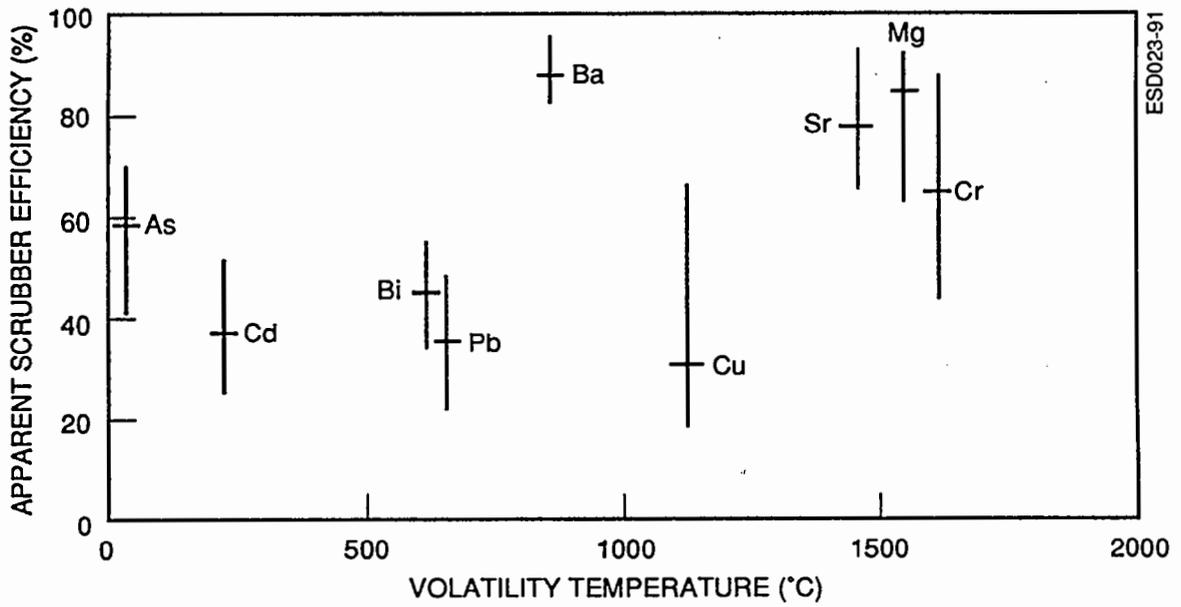


Figure 8. Apparent collection efficiencies for metals achieved by the venturi/packed-column scrubber.

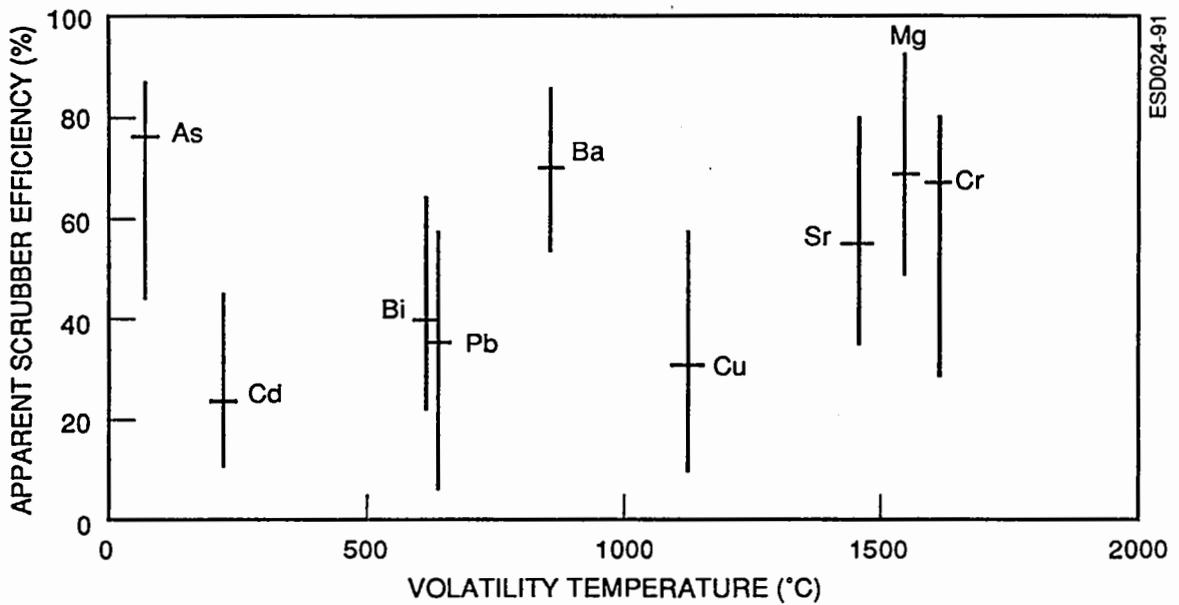


Figure 9. Apparent collection efficiencies for metals achieved by the single-stage ionizing wet scrubber.

- Lead behavior in the rotary kiln differed between the two test series. For the venturi/packed-column test series, the average fraction of lead discharged to the kiln ash was 20 percent. For the ionizing wet scrubber test series, the average fraction of lead discharged to the kiln ash was 82 percent. This inconsistent behavior may be related to the strong relationship between lead volatility temperature and chlorine or to the sensitivity of lead volatility to temperature over the range tested.
- Relative metal volatilities in the kiln generally agreed with expectations based on metal volatility temperatures, with the exception of arsenic, which was much less volatile than expected. It is possible that arsenic forms a thermally stable compound in the incineration environment or becomes physically bound in the solid matrix.
- Results from the ionizing wet scrubber test series showed that increased kiln temperature caused increased volatility of bismuth, cadmium, and lead. There was a significant decrease in the kiln ash fraction of these metals, with corresponding increases in the scrubber exit flue gas and scrubber liquor fractions. Discharge distributions of the remaining metals were insensitive to changes in kiln temperature.
- Afterburner temperature did not affect metal distribution to the scrubber exit flue gas and scrubber liquor discharge streams.
- Increased feed chlorine content caused increased volatility of copper and lead during the venturi/packed-column test series. There was a significant decrease in the kiln ash fraction of these metals, with corresponding increases in the scrubber exit flue gas and scrubber liquor fractions. Discharge distributions of the remaining metals did not vary conclusively with changes in feed chlorine content. Also, variations in feed chlorine content did not conclusively affect any metal discharge distributions during the single-stage ionizing wet scrubber test series.
- Both kiln temperature and feed chlorine content affected the distributions of at least some of the metals among the flue gas particulate in the less than 10  $\mu\text{m}$  size range. Size distributions of the metals most nearly reflected the overall entrained particulate size distribution for the tests with the lowest kiln temperature and no chlorine in the waste feed; very little redistribution among the particulate was observed. For these two tests, approximately 20 to 25 percent of each metal and of the total particulate sample were in the less than 10  $\mu\text{m}$  particulate.
- Increasing the kiln temperature to 927°C (1700°F) caused the average size distribution to shift to approximately 60 percent less than 10  $\mu\text{m}$  for all test metals except chromium. The test data suggest that increased kiln temperature over this range caused the flue gas particulate metal distributions to shift to the finer particulate size fractions. Additionally, the redistribution of metals to this size range generally correlated with the relative volatilities of the metals, with the volatile metals most affected. Interestingly, arsenic in the flue gas behaved as the most volatile metal, becoming most enriched in the less than 10  $\mu\text{m}$  particulate size range. Test data show that even metals that are classified as relatively nonvolatile based on their behavior in the kiln undergo some vaporization and recondensation, with resulting concentration in the finer particulate size range.

- The addition of chlorinated compounds to the waste feed primarily affected cadmium, chromium, copper, and lead distributions in the flue gas particulate less than 10  $\mu\text{m}$ . For cadmium, copper, and lead, the increase in waste feed chlorine content from 0 to 4 percent caused the distributions to shift from roughly 20 percent to approximately 55 percent less than 10  $\mu\text{m}$ . No further effects with feed chlorine increased to 8 percent were observed for these metals. For chromium, increased chlorine content from 0 to 4 to 8 percent caused redistributions of 2 to 20 to 50 percent in the particulate less than 10  $\mu\text{m}$ .
- Average metal collection efficiencies for the venturi/packed-column scrubber ranged from 31 to 88 percent; the overall average for all metals was 57 percent. For the single-stage ionizing wet scrubber, average metal collection efficiencies ranged from 22 to 71 percent; the overall average for all metals was 43 percent. In general, collection efficiencies were higher for the less volatile metals.

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## SOIL HEATING TECHNOLOGIES FOR IN SITU TREATMENT: A REVIEW

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### ABSTRACT

In the remediation of soils contaminated with hazardous compounds, the costs, logistical concerns, and regulatory requirements associated with excavation, ex situ treatment, or off site treatment make in situ treatment a highly attractive alternative. Because temperature affects a number of physical, chemical, and biological processes in soils, the effectiveness and efficiencies of some in situ treatment technologies can be improved by controlling soil temperature. Technologies such as bioremediation and gas phase removal of organic compounds, for example, can be enhanced through heating of the soil. Consequently, there is great interest in the development and testing of methods of soil heating to be used in conjunction with in situ treatment technologies. This paper reviews temperature effects and various ways that heating is being incorporated into in situ remediation of contaminated sites.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

The U.S. EPA's Superfund research program is developing methods for in place (in situ) removal of contaminants from soils and for in place treatment of contaminated soils. This work is motivated by the high cost of managing large volumes of soil with low levels of contamination and by the need to comply with provisions of the Superfund Amendments and Reauthorization Act (SARA) and the Resource Conservation and Recovery Act (RCRA).

A recent U.S. EPA report (U.S. EPA, 1990a) on in place treatment describes a large number of chemical and physical processes (e.g. oxidation, reduction, precipitation) that could potentially be used in situ to immobilize or detoxify contaminants in soils. The majority of these are conceptual or have been tested only in the laboratory. Although in place chemical treatments involving these processes have been proposed, the major developments have been in biodegradation, stabilization/ solidification, and removal of contaminants in the gas phase. Many chemical/ physical/ biological processes in soil are affected by temperature to some degree. Consequently, U.S. EPA is investigating methods for heating soil in place to affect these processes and make in situ treatments more effective.

## TEMPERATURE EFFECTS

Temperature dependent chemical/physical phenomena that affect the efficiency of in situ treatment processes include vapor pressure, mass transfer coefficients, equilibrium constants, and reaction velocity/rate constants. Co-distillation of immiscible compounds and movement of water and gases in unsaturated soils are other relevant phenomena affected by temperature.

It is well known that vapor pressure of liquids increases with increasing temperature (Maron and Prutton, 1965). This allows increases in temperature to increase the rate of removal of individual organic compounds in the gas phase. It also allows gas phase removal of compounds that do not have a sufficiently high vapor pressure at normal soil temperatures. Increasing temperature also increases the diffusion coefficient and, hence, the rate of diffusion in the gas phase as well as the liquid phase (Call, 1957; Elhers *et al.*, 1969; Lavy, 1970). In situ radio frequency heating and in situ vacuum-assisted steam stripping both take advantage of this effect for removal of organic compounds in the gas phase.

The mass transfer coefficient for oxygen across the air-water interface increases approximately linearly with increasing temperature in the range 0 to 35° C (Downing and Truesdale, 1955). Temperature also affects the magnitude of coefficients for transfer of other chemicals across this interface (Thibodeaux, 1979).

Compounds with low water solubility (e.g. PCB, pentachlorophenol) will volatilize in the presence of boiling water at temperatures lower than their boiling points as pure compounds (Maron and Prutton, 1965). This

phenomenon, called steam distillation or co-distillation, enhances the effectiveness of in situ radio frequency heating and in situ vacuum-assisted steam stripping for removal of organic compounds in the gas phase.

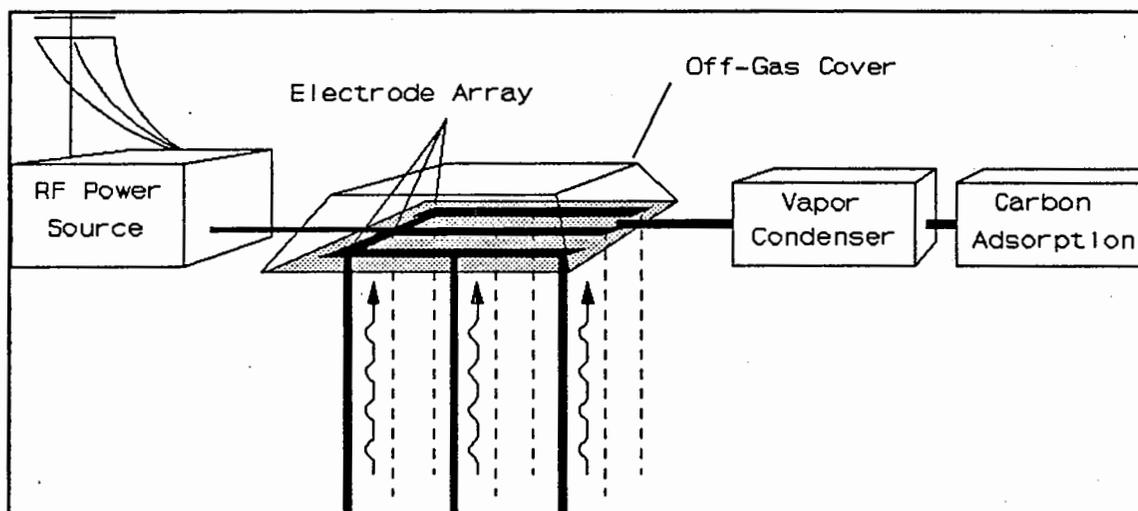
Chemical treatment of contaminated soil in situ has been envisioned (U.S. EPA, 1990a) but has not yet been applied to any significant extent. As in situ chemical treatments are developed it will be possible to take advantage of the increases in reaction velocity/rate constant and the changes in equilibrium constants for most chemical reactions with increasing temperature (Maron and Prutton, 1965). The only application of this effect in situ has been the investigation of radio frequency heating for use in soil to facilitate potassium polyethylene glycolate (KPEG) treatment of chlorinated organics such as PCB (Dev, 1986).

Temperature gradients in unsaturated soil have a small but appreciable effect on the rates of movement of water (Letey, 1968). Water moves along the temperature gradient, i.e. from areas of high temperature to areas of lower temperature. It may be possible to use the temperature gradient effect to aid in distribution of treatment chemicals in situ.

Temperature has a profound effect on the activity of microorganisms in soil and this effect can be used to great advantage during in situ bioremediation. Most microorganisms grow only within a limited temperature range; maximum and minimum growth temperatures are about 30° C apart. The optimum temperature for growth of mesophiles is about 38° C; the optimum for thermophiles is about 62° C (Tortora *et al.*, 1989). Soil heating can be used to improve the growth rates of these classes of organisms because their optimum temperatures are well above normal soil temperatures. This makes it possible to shorten the time required for in situ bioremediation by heating the soil. In areas of colder climate it may not be possible to conduct in situ bioremediation during much of the year because of low soil temperatures. Artificially warming the soil can extend the time during which bioremediation is effective and thus shorten the overall time for remediation. Finally, it may be possible to favor the activity of specific organisms if their optimum temperature is higher than the optimum for competing organisms.

#### RADIO FREQUENCY HEATING

The in situ radio frequency (RF) heating method allows relatively rapid and uniform in place heating of large volumes of soil in the vadose zone. The heating is performed by the application of electromagnetic energy in the radio frequency band. The temperature rise occurs due to ohmic or dielectric heating mechanisms and does not rely on thermal conductivity of the soil matrix. As shown in Figure 1, electrodes are inserted into the contaminated soil through drilled bore holes. The electrode array consists of three rows of electrodes inserted to the depth of the zone to be decontaminated. RF power is applied to the center row of electrodes, and the two outer rows serve to confine the energy within a



**Figure 1. Radio Frequency Heating**

defined volume of soil. The soil is heated volumetrically and uniformly to temperatures between 150° C and 300° C. In this temperature range many volatile and semivolatile hazardous organic compounds can be vaporized. Vaporized native soil moisture and contaminants are collected and treated on site through a soil vapor extraction and treatment system. The contaminant vapors and boiled water are recovered by the application of a vacuum to selected hollow electrodes, which have been specially designed to allow both the application of RF power to the soil and the collection of vapors from the soil. The collection electrodes are connected to a vacuum manifold which transports the gases and vapors to an on-site treatment system where vapors may be condensed and uncondensed gases may be treated by carbon adsorption, combustion, or scrubbing. An additional component of the system is generally a rubber sheet barrier laid out over the soil surface. It serves to prevent fugitive emissions and to provide thermal insulation to avoid excessive cooling of the near surface zone.

In addition to the usual advantages of a process that works in situ as opposed to ex situ (above ground), RF heating has several other attractive points. For instance, the process produces only one one thousandth the amount of fluids, gases, and liquids produced by incineration. Uniformity of heating allows more uniform decontamination than some alternate technologies. Furthermore, researchers claim the technique can handle variations in the soil matrix, such as soil moisture and clay stringers present in sandy soil. It may also be more effective than certain other technologies in remediating clayey soils, which are often more difficult to decontaminate than sandy soils.

A number of bench- and pilot-scale RF tests as well as limited field testing have been performed (Dev and Downey, 1988; Dev et al., 1984; Dev et al., 1986; Dev et al., 1988; Dev et al., 1989; Anonymous, 1988). A field test was conducted on hydrocarbons at the Volk Air National Guard Base (Dev

and Downey, 1988; Dev *et al.*, 1989; Anonymous, 1988). Table 1 summarizes various test results (Sresty *et al.*, 1990). Removal efficiencies of up to 99% have been obtained. Further field demonstration is planned (Sresty *et al.*, 1990). The in situ RF heating decontamination technology is also being offered on a commercial basis (Anonymous, 1989).

**TABLE 1. SUMMARY OF DECONTAMINATION TESTS USING RADIO FREQUENCY HEATING TECHNOLOGY**

Soil Type	Contaminants	Conc. Range, ppm	Treatment Time, hr.	Type of Exper.	Results % Removal
Sandy	Tetrachloro-ethylene	10, 1000	4 16	Bench Pilot	94 to 98 94 to 98
Sandy	Chlorobenzene	10, 1000	4 16	Bench Pilot	94 to 98 94 to 98
Sandy	Jet fuel, solvents	1-5000	16-24 12 days	Pilot Field test	91 to 99 94 to 99
Sandy	Aroclor 1242	1000	16	Pilot	70 to 99.8
Clayey	Jet fuel, solvents	1-1000	16-48	Pilot	70 to 98.3

Source: Sresty *et al.*, 1990

#### STEAM AND HOT AIR STRIPPING

In situ steam stripping or hot air stripping or a combination of the two have also been used to recover highly to moderately volatile organics from contaminated soil. Contaminants with boiling points less than 250° C are most amenable. Heat from injected steam or hot air assists in vaporization of the compounds, while the gas flow carries the contaminants to the soil surface. A vacuum can accelerate the rate of volatilization and speed the transport of contaminants to the surface as well as guard against leakage to the outside environment. The off gases are then pulled through an above-ground treatment train, for example, condensers followed by carbon adsorption. Figure 2 represents a generalized typical system.

Several diverse studies and tests of the technology have been reported. In one case, a field pilot test was performed to investigate the advantages of piping waste heat from a catalytic incinerator to a site contaminated with hydrocarbons (DePauli, 1990). Tests indicated an improvement of 70% in total hydrocarbon removal due to hot air injection. In New Mexico a hot air injection system is being used to increase biodegradation rates for in situ remediation of leaking underground storage

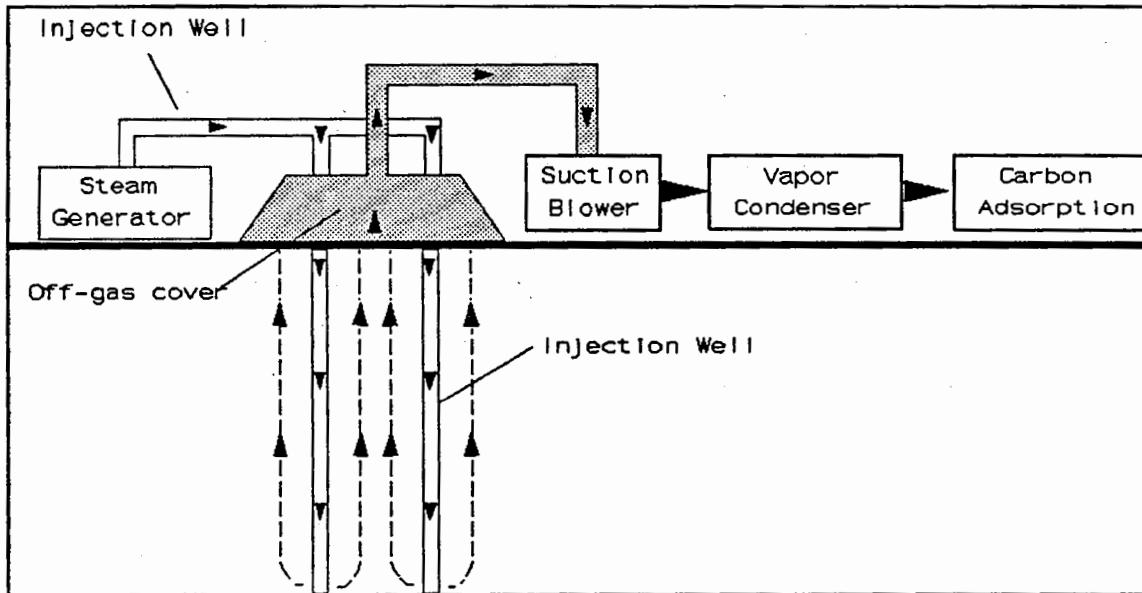


Figure 2. Vacuum-Assisted Steam Stripping

tanks (Hinchee and Smith, 1990a). Lord *et al.* (1988, 1989, 1990) conducted laboratory studies of vacuum-assisted steam stripping of organic contaminants from soils. An analytical model was developed to determine some basic parameters. Small-scale experiments were run employing a geosynthetic cap to facilitate the confinement and collection of steam and contaminants. Effects of varying steam pressures on contaminant removal efficiencies were also investigated. Nunno *et al.* (1989) reported that several field tests of an in situ steam stripping process were conducted on contaminated soil in the 1980s in the Netherlands with varying levels of success. Looking at a possible variation to the steam stripping process, Jackson *et al.* (1990) performed a literature review to investigate the technical feasibility of using surfactants to enhance in situ steam stripping processes for removing organic compounds from contaminated soils. Laboratory-scale experiments to investigate the use of surfactants with steam stripping were planned. Steam injection combined with vacuum extraction was tested at pilot-scale at a site in San Jose, California (Udell and Stewart, 1989; Baum, 1988). Soil at the site contaminated with several organic solvents was successfully cleaned to a low part per million level. Some contaminants were recovered in quantities sufficient to make recycling of them back into commercial chemical use feasible. A combination steam and hot air stripping technology was demonstrated in situ in U.S. EPA's Superfund Innovative Technology Evaluation (SITE) Demonstration Program in 1989. This system used rotating augers to break up and mix the soil as well as to inject steam and hot air. At the site in San Pedro, California, twelve blocks of soil approximately 7 ft. by 4 ft. were treated to a 5 ft. depth. Removal efficiencies for volatile organic compounds averaged 85%. Semivolatile organic compounds were also removed, but at a lower efficiency (U.S. EPA, 1990b; de Percin, 1990). This same

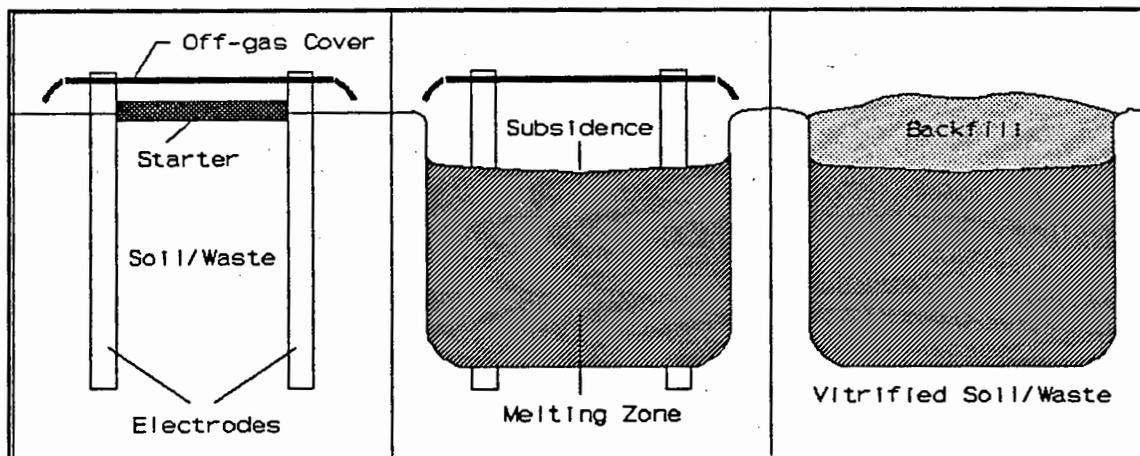
system is capable of injecting remediation agents, such as stabilizers or chemicals, and mixing them into the soil (La Mori, 1989). A process being studied in U.S. EPA's SITE Emerging Program uses enhanced oil recovery technology to recover a major portion of the organic liquid phase in subsurface oily waste accumulations. The oily waste is mobilized by in situ heating with steam and is displaced to production wells by sweeping with hot water. Residual contaminants not recovered are subsequently treated by in situ microbial degradation. Laboratory-scale studies of the technology have been performed (Johnson and Guffey, 1990; U.S. EPA, 1989).

## VITRIFICATION

In situ vitrification (ISV) is a soil heating technology in which a powerful current of electricity is transferred within a square array of electrodes that are inserted into contaminated soil at the desired treatment depth. A layer of graphite is then applied within the area of the electrodes on the ground surface to act as a starter path. Because dry soils are not electrically conductive, the graphite acts as a starter to initiate a melting zone in the contaminated soil. The melting zone (generally about 1600°C to 2000°C ( 2900°F to 3600°F)) caused by this electrical current gradually works its way downward and outward (past the electrodes) melting the contaminated soil. As the melting action is taking place, the pyrolyzed by-products migrate to the surface of the vitrified zone and burn in the presence of air. Evolved gasses are trapped under an off-gas cover placed on the top of the treatment area and sent to a treatment unit to ensure that emissions are within regulatory limits. When the process is terminated the contaminated soil cools into a stabilized crystalline block, with about ten times the strength of unreinforced concrete (see Figure 3). It is not affected by either wet/dry or freeze/thaw cycling and passes EP-Tox and TCLP leach testing criteria for priority pollutant metals (Buel *et al.*, 1987).

A large scale ISV system, with a maximum electrode array of 30 ft. width by 30 ft. depth, can produce a soil melt rate of 4 to 6 tons per hour and can encompass a total melting zone of 1000 tons of contaminated soil. Generally, the melt grows outward to form a melting zone approximately 50% wider than the electrode array. Recent testing has shown that organic and other vapors are not driven outward by the heat of the ISV process but rather migrate toward the melt and toward the surface of the melt (Hansen *et al.*, 1990). As the void volume in the soil can account for 20 to 40% of the volume, a proportionate volume reduction occurs when the melting zone is vitrified. This subsidence can then be covered with clean backfill and vegetated.

The contaminated soil conditions have a direct bearing on the ISV melting process and the quality of the vitrified block. This technology is most effective on low moisture soils. If groundwater is present and soil permeability is less than  $1 \times 10^{-5}$  cm/sec, additional energy must be expended in order to drive off the water to heat the soil. Typical soils require 800 to 1000 kwh/ton total energy input, which can be supplied by local utilities or be diesel-generated in remote locations. ISV processing



**Figure 3. In Situ Vitrification**

requires relatively high levels of glass forming materials, such as silica (50-80%) and alumina (5-12%), in the soil to form and support a high temperature melt. Sufficient levels (2 to 5%) of monovalent alkali cations, such as sodium and potassium, must also be present to provide the electrical conductivity needed to advance the heat rate in the contaminated soil. Most of the soils tested for ISV processing (in 30 out of 32 cases) have been found to contain adequate levels of these materials (Hansen et al., 1990).

This technology can potentially treat a wide range of contaminants. It is therefore possible that mixtures of organic, inorganic, and radioactive contaminants in a solid media could be processed simultaneously. Organic contaminants are destroyed by pyrolysis and are expected to be most effectively treated at concentrations in the 5 to 10 percentage-of-weight range. Inorganic contaminants are then incorporated into a vitrified residual product and are expected to be most effectively treated at the 5 to 15 percentage-of-weight range. Site conditions that may limit applicability of the ISV process are 1) individual void volumes in excess of 150 cubic feet, 2) metals in excess of 5 percent of the melt weight or continuous metal occupying 90 percent of the distance between the electrodes, 3) rubble in excess of 10 percent by weight, and 4) combustible organics in the soil or sludge (U.S. EPA, 1989).

The ISV technology was originally created and applied to stabilize radioactive and radioactive mixed wastes, and has been applied as a large-scale test at the Department of Energy's (DOE) Hanford site. It has however, recently gained interest for the treatment of hazardous waste. The first such application of ISV is currently being performed at a private site contaminated with PCBs. Superfund sites slated for ISV processing this year include, Parsons/ETM (EPA), Denver Radium (EPA), Ionia City Landfill (EPA/PRPs), Northwest Transformer (EPA/PRPs), M-1 Ponds (Army), and Site 10 (Air Force).

Cost estimates for this technology range from \$275 to \$600 per ton of treated soil, depending on the site characteristics.

#### ELECTRICAL RESISTANCE HEATING

Electrical resistance heating technology heats soil by passing an electrical current through electrodes that are inserted into ground (Heath, 1990). Unlike in situ vitrification, however, no melting action of the soil takes place to stabilize contaminants. Enough current is applied through the electrodes to remove most of the soil moisture and volatile contaminants. Once the soil moisture is driven off by the heat (approximately 65°C (150°F)), the voltage is increased to stimulate in place oxidation of any nonvolatile organics which are then transformed into lighter components that volatilize. During the process, all water vapor and volatiles are collected using conventional vacuum extraction techniques.

While electrical resistance heating has been employed at the pilot scale for the melting of permafrost, it has only recently been explored at the bench scale for in situ treatment of contaminated soils. During experimentation, however, there was an approximately 90% removal of volatile and semivolatile/nonvolatile materials tested which makes this technology a potentially efficient way to treat contaminants in situ through soil heating (Hinchee and Smith, 1990b).

#### SOIL PROPERTY MODIFICATION

Heating through modification of the soil properties can produce only small temperature increases but the methods are simple and no additional energy inputs are required, making this a "low-tech" approach to soil heating. Modification of surface properties regulates the incoming and outgoing energy, increasing the heat absorption of the soil during warm or sunny periods and reducing heat loss during cold or dark conditions. This is achieved by the use of plastic sheeting, stripping surface vegetation, or applying organic mulches to the ground surface (Hinchee and Smith, 1990c). The soil can also be irrigated to increase thermal conductivity and the net heat transfer into the soil.

Clear polyethylene sheets applied to a stripped soil surface are used to increase radiation collection during the day and reduce convective and conductive heat loss at night. In Alaska, where this technology has been tested at the pilot scale level for applications to improve crop growth and melting permafrost, clear polyethylene has produced positive results. A soil temperature increase of 16.7°C (30°F) at a depth of an inch was achieved using clear polyethylene to improve increased crop yield and seed germination (Dinkel, 1966). In testing to melt permafrost (Nicholson, 1978), small plots were tested with a variety of soil surface applications and produced the following soil temperature increases:

- o 2°C (3.6°F) for stripping vegetation

- o 4.5°C (8°F) for clear polyethylene over natural vegetation
- o 5.5°C (10°F) for clear polyethylene over stripped vegetation.

Increasing soil water content by irrigation increases the heat capacity of the soil, raises the humidity of the air, lowers air temperature over the soil, and increases thermal conductivity. The cumulative result is a reduction in daily soil temperature variations and an increase in the net heat transfer into the soil (Baver et al., 1972).

Soil property modification can provide in situ heating at a low cost and is a viable supplement for bioremediation, particularly in colder climates. Because temperature increases are nominal and can often take days and weeks to attain, this concept could not achieve the high temperatures required to significantly increase vapor pressures and promote removal of contaminants in the gas phase. To date, however, none of the soil surface modification concepts have been demonstrated for remediation at contaminated sites.

### SOLAR HEATING WITH OPTICAL FIBERS

The sun is a low intensity source of energy for soil heating; under ideal conditions the power density available from the sun is about one kilowatt per square meter of collector. Parabolic collectors coupled to optical fibers are another method that is being tested for using solar energy to heat soil in situ. Collectors have been used in the past for direct heating of air and water. There are significant heat losses during transmission that would make this process undesirable for in situ heating of soil. An approach to overcoming these heat losses during transmission is being tested in a research project (Brown and Murdoch, 1990) that was started in July 1990.

Compound parabolic concentrators, which have the advantage of collecting scattered sky light as well as direct sunlight, are being modified for coupling to a cable of optical fibers. The optical fiber has the potential to transfer the solar radiation with high efficiency over long distances. By conducting the solar energy as light, rather than as a hot fluid, thermal losses along the transmission line are eliminated. The collector surfaces also remain relatively cool and radiate away little energy because conversion to heat occurs at the radiator or the end of the optic cable, rather than at the collector.

Two problems must be resolved to allow development of a workable and efficient system. The coupling between the optical cable and the solar collector must transmit energy without causing sufficient temperature increase to damage the cable. The shape of the collector must also be designed to capture the maximum energy without requiring an elaborate tracking system. The shape of the collector also affects the transfer of energy to the optical cable through the coupling; some parabolic collectors are so sharply focused that local melting of the cable cannot be prevented with any of the available couplings.

In addition, the project is collecting and evaluating information on heat transfer in soils to determine whether projected power inputs from solar collectors coupled to optical fibers will be capable of achieving satisfactory heating rates and maximum temperatures in soil.

#### CONCLUSIONS

There are a number of physical, chemical, and biological processes in soils that are affected by temperature; this temperature effect can be used to advantage for improving the efficiency of in situ treatment technologies. A number of methods for heating soil have been developed or adapted from other applications; most of these have been tested in conjunction with one or more in situ treatment technologies. Soil heating has been used to enhance bioremediation and gas phase removal of organic compounds. In situ soil heating could potentially be applied to enhance the performance of other technologies such as chemical treatment but has not yet been used for this purpose.

#### ACKNOWLEDGMENTS

The authors wish to thank Robert E. Hinchee and Lawrence A. Smith of Battelle, Columbus, OH, who contributed to the literature review for this paper under work assignment 0-09, Contract 68-CO-0003.

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THE UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
MUNICIPAL WASTE COMBUSTION RESIDUE  
SOLIDIFICATION/STABILIZATION PROGRAM

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ABSTRACT

Vendors of solidification/stabilization (S/S) and other technologies are cooperating with the U.S. Environmental Protection Agency's (U.S. EPA's) Office of Research and Development (ORD), Risk Reduction Engineering Laboratory to demonstrate and evaluate the performance of the technologies to treat residues from the combustion of municipal solid waste (MSW). Solidification/Stabilization is being emphasized in the current program. This technology may enhance the environmental performance of the residues when disposed in the land, when used as road bed aggregate, as building blocks, and in the marine environment as reefs or shore erosion control barriers.

The program includes four S/S process types: cement, silicate, cement kiln dust and a phosphate based process. Residue types being evaluated are fly ash, bottom ash and combined residues. An array of chemical leaching tests and physical tests are being conducted to characterize the untreated and treated residues. This paper discusses program design, status and preliminary results.

The S/S evaluation program is the first part of ORD's Municipal Solid Waste Innovative Technology Evaluation (MITE) program.

## INTRODUCTION

During the past two years there has been a significant concern expressed about the management of the residues from the combustion of municipal solid waste. Much of this concern has centered on the fact that when the residues are subjected to the Extraction Procedure for Toxicity (EP tox) and the Toxicity Characteristics Leaching Procedure (TCLP) they will fail for lead and cadmium a significant portion of the time. This occurs more often for the fly ash, less for the combined fly ash and bottom ash, and least often for the bottom ash alone. Because of this, a controversy exists as to whether or not the residues should be considered and regulated as a hazardous waste or exempted because they originated from burning municipal solid waste. Several states are requiring that these residues be disposed into landfills with designs and operating procedures as, or more, stringent than those for hazardous waste. Municipal Waste Combustion (MWC) ash characteristics are extremely variable as is the leachate from these ashes. Ranges of metal concentrations observed in bottom and fly ashes from many sources are presented in Table 1<sup>(1)</sup>. Detailed descriptions of the chemical and physical characteristics of MWC residues are available<sup>(2,3,4,5)</sup>.

TABLE 1. RANGES OF TOTAL AND LEACHABLE METALS IN UNITED STATES MSW COMBUSTOR ASH AS DETERMINED BY RESEARCHERS<sup>(1)</sup>

Com-pound	Bottom Ash mg/kg	Bottom Ash Leachate mg/l	Fly Ash mg/kg	Fly Ash Leachate mg/l
Pb	31 - 36,600	0.02 - 34	2.0 - 26,000	0.019 - 53.35
Cd	0.81 - 100	0.018 - 3.94	5 - 2,210	0.025 - 100
As	0.8 - 50	ND(0.001) - 0.122	4.8 - 750	ND(0.001 - 0.858)
Cr	13 - 1,500	ND(0.007) - 0.46	21 - 1,900	0.006 - 0.135
Ba	47 - 2000	0.27 - 6.3	88-9000	0.67 - 22.8
Ni	ND(1.5) - 12,910	0.241 - 2.03	ND(1.5) - 3,600	0.09 - 2.90
Cu	40 - 10,700	0.039 - 1.19	187 - 2,300	0.033 - 10.6

ND = Not Detectable; ( ) = Detection Limit

Because of the growing concern about the residues and anticipating the need for appropriate treatment techniques, the Office of Research and Development designed and implemented a program to evaluate the use of solidification/stabilization technologies for treating the residues. The program was formally announced on September 19, 1989. Originally known as the U.S. EPA MWC Ash Solidification/Stabilization Evaluation Program, it is now the Municipal Innovative Technology Evaluation program (MITE). This paper presents the design and status of the current program.

## THE MITE PROGRAM

The MITE program is an Office of Research and Development (ORD) program designed to conduct demonstrations of technologies for managing municipal solid waste. The objective is to encourage development and use of innovative technology for municipal solid waste management. The program is patterned after the Superfund Innovative Technology Evaluation program (SITE). It is, therefore, a cooperative program in which the technology developer and/or vendor pays the cost of conducting the demonstration. U.S. EPA pays the cost of testing and evaluation, including analytical cost. U.S. EPA will report the results of the evaluations in an unbiased manner, thus providing a means for assisting municipalities and others to better evaluate and select technologies more appropriate for their given situation.

The current program is demonstrating and evaluating alternatives for the treatment of residues from the combustion of municipal waste. While it is uncertain if treatment will be required prior to disposal, it is most likely that treatment will be necessary for any utilization option. Solidification/Stabilization technology was selected for initial evaluations based upon experience and knowledge of the technology for treating hazardous waste and experimental studies on solidifying municipal waste combustion (MWC) residues<sup>(6)</sup>. Solidification/Stabilization, in general terms, is a technology where one uses additives or processes to transform a waste into a more manageable form or less toxic form by physically and/or chemically immobilizing the waste constituents. Most commonly used additives include combinations of hydraulic cements, lime, pozzolans, gypsum, silicates and similar materials. Other types of binders, such as epoxies, polyesters, asphalts, etc. have also been used, but not routinely. More detailed descriptions of S/S technology are available<sup>(7)</sup>. The program objective is to provide a credible data base on the effectiveness of S/S technology for treating the residues.

Preliminary design of this program was completed by the U.S. EPA. Because U.S. EPA believed it important to have results completely unbiased and as scientifically credible as possible, a panel of international experts was assembled to provide oversight to the program. This Technical Advisory Panel (TAP) consists of experts from academia, industry, state and federal governments, and environmental groups.

### PROGRAM ORGANIZATION AND DESIGN

Organization - The program involves the participation of several different organizations with separate roles. The Risk Reduction Engineering Laboratory (RREL) is managing and directing the program. The TAP is providing valuable peer review, oversight and technical design. This service is donated. Staff at the U.S. Army Corps of Engineers Waterways Experiment Station (WES) are coordinating and observing the demonstrations at WES facilities located in Vicksburg, Mississippi. WES is also responsible for performing the physical testing and some of the extraction/leaching tests. A laboratory experienced in MWC residue analysis is performing the majority of the analytical work. Specialized analyses, testing and modeling is being performed by the University of Illinois and the Netherlands Energy Research Center. Rutgers

University in conjunction with the New Jersey Institute of Technology is assisting in the coordination of the various activities and participants. Vendors are participating by providing valuable time and money.

Tests and Analyses - The program was conceived by U.S. EPA and the basic design was based on the testing and evaluations performed on hazardous and other waste treated by solidification/stabilization technologies in various research and evaluation programs of U.S. EPA. At the request of U.S. EPA, the TAP reviewed and modified this preliminary design. The tests and analytical protocols included in the program are provided in Tables 2, 3, 4, 5, 6 and 7. The purpose for conducting the test and analysis listed is also included. Methods listed in the Tables are either approved U.S. EPA or ASTM methods.

TABLE 2. CHEMICAL ANALYSIS PERFORMED ON TREATED AND UNTREATED ASH

Assay	Method	Purpose
Total Extractable Metals	3050, 6010	See Metals Analysis List (Table 6)
Dioxins/Furans	8280	Community Concern (Untreated Only)
pH, Anions, Total Available Dissolved Solids, and Ammonia	9045, 300.0, 160.1, 350.2	Salts and Ionic Species
Loss on Ignition	209D	Residual Organic Matter (typ. 2-5%) and Water of Hydration
Chemical Oxygen Demand	508A	Reduced Inorganic and Organic Matter
Total Organic Carbon		Residual Organic Matter

Summary of Leach Tests - For information, following is a summary of three leach tests used:

- Availability (static pH) - The availability leach test was developed by the Netherlands Energy Research Foundation to quantify the maximum amount of a species which could be released to the environment under assumed worst case conditions during the lifetime of the material. The test does not provide information on release rate or anticipated natural leachate concentrations. The test is carried out using two serial extractions of the material to be tested. The sample to be tested is crushed to less than 300 microns and extracted at constant pH 7 for the first extraction and pH 4 for the second extraction at a liquid to solid ratio of 100:1 for each step. Extraction pH is maintained through use of a pH controller delivering dilute nitric acid.

- Distilled Water Leach Test - The distilled water leach test is designed to estimate species release during contact with uncontaminated natural waters. The test is carried out by serially contacting material crushed to less than 2 mm with distilled water four times. The liquid to solid ratio for each contacting is 10:1. The pH of the system is established for the material being tested (typically alkaline for solidified MWC residue). The first and second extracts (extracts 1 and 2) were combined for analysis, as were extracts 3 and 4, to minimize analytical costs.
- Monolith Leach Test - The monolith leach test was carried out to assess the rate of species release from solidified/stabilized MWC residues. A cylindrical sample (4 cm dia by 4 cm) is contacted with distilled water for up to 64 days. Contacting water is replaced at 1, 2, 4, 8, 16, 32 and 64 days and is analyzed. Modeling of release data will establish effective diffusion coefficients for estimating long term species release rates. This leach test is a modified version of ANSI 16.1.

Ash Types Tested - Residue selected for testing was limited to that collected from a modern state-of-art waste to energy facility (i.e., high burn out, lime scrubber with fabric filter, etc.). There were several reasons for limiting the number of residues included in the program. The prime objective is to evaluate solidification/stabilization for treating the residues, rather than determine how characteristics of different residues may affect the performance of the technology. In addition the apparent variability of MWC residues is becoming less of an issue, especially with the newer combustion facilities. Proper sampling and analysis, changes in air pollution controls and similar factors will play more important roles in the variability of residues. The program currently includes four different S/S process types plus one control. Because of the extensive list of tests being performed, the analytical cost for the program is the major U.S. EPA expense. For each additional source of residue added these costs must be duplicated. This would have reduced the number of processes which could be evaluated to an unacceptable number. The program is also developing and evaluating testing protocols that can be used to evaluate selected S/S processes on different residues if required in the future.

These considerations quickly led to the conclusion that the program would test the residue from only one facility. The residue types are the fly ash (including the scrubber residue), the bottom ash and the combined ash. The MWC facility has the following process sequence: (i) primary combustor with vibratory grates, (ii) secondary combustion chamber, (iii) boiler and economizer (iv) dry scrubber with lime, and (v) particulate recovery using baghouses (fabric filters). Bottom ash sampled was quenched after exiting from the combustion grates. Fly ash sampled was mixed residuals from the scrubber and baghouses. The fly ash was screened to pass a 0.5 inch square mesh. The bottom ash and combined ash were screened to pass a 2 inch square mesh at the MWC facility. Materials not passing through the 2 inch mesh were rejected. After shipment to the WES, each ash type was dried to less than 10% moisture, crushed and screened to pass a 0.5 inch mesh (nominally 3/8 inch after clogging), and homogenized.

TABLE 3. PHYSICAL TESTS CONDUCTED ON TREATED AND UNTREATED ASH

Physical Test	Purpose
Moisture Content	Useful general data
Loss on Ignition	Residual/Organic Matter and Hydrated Water
Modified Proctor Density	Compressibility
Bulk Density	Volume and Similar Physical Changes
Particle Size Distribution	Potential Use as Aggregate
Cone Penetrometer	Curing Rate and Hardness
Pozzolanic Activity*	Untreated S/S Potential
Porosity/Surface Area	Potential for Liquid-Solid Contact and Diffusion Effects
Permeability	Resistance to H <sub>2</sub> O Transmission; Assist in Determining Contaminant Release Mechanisms
Unconfined Compressive Strength (UCS)	Load Bearing Capacity
UCS after Immersion	Hydration Effects and Swelling
Freeze/Thaw**	Physical Weathering Effects
Wet/Dry**	Physical Weathering Effects

\* Untreated Ash Only

\*\* Treated Ash Only

Processes Selected - Process types selected in the program are cement based, silicate based, cement kiln dust and phosphate based. A non-vendor cement process is being performed by experienced staff of WES and U.S. EPA in Vicksburg, MS.

Process selection was competitive based upon evaluation of proposals submitted by parties interested in participating. A formal Request For Participation was issued by U.S. EPA which provided information required to respond. Under direction of U.S. EPA, the TAP developed evaluation criteria which was used to make final selections.

TABLE 4. LEACHING TESTS FOR TREATED AND UNTREATED ASH

Leach Test	Purpose
TCLP (1 extract)	Regulatory Leach Test <sup>8</sup>
Distilled Water Leach Test (4 extracts)	Extended Extraction in a Well-Mixed System without Acid
Acid Neutralization Capacity (10 extracts)	Buffering Capacity of Solid and pH Dependence of Metals Release
Monolith Leach Test (7 extracts)	Estimate Potential Release Rates Through Diffusion
Static pH @ pH = 4.0 with HNO <sub>3</sub> Liquid:Solid Ratio is 100:1	Total Species Available for Release Under "Worst Case" Scenario

TABLE 5. CHEMICAL ANALYSIS PERFORMED ON LEACH TEST EXTRACTS

Assay	Method	Purpose
Metals	3020	See Metals Analysis List (Table 6)
Chemical Oxygen Demand (COD)	508A	Surrogate for Leachable Organic Species
Total Suspended Solids	160.2*	Physical Erosion of Solid
Total Dissolved Solids	160.1	Leachable Total Salts
pH	150.1	

\* Monolith leach test only (ANSI 16.1)

TABLE 6. LIST OF METALS SUBJECTED TO ANALYSIS

<u>Metal</u>	<u>Untreated and Treated</u>		<u>Extracts</u>
	<u>Ash (Solid)</u>		
	<u>ICP or AA</u>	<u>Neutron</u> <u>Activation</u>	<u>ICP or AA</u>
Aluminum	X	X	X
Antimony	---	X	X
Arsenic	X	X	X
Barium	X	X	X
Beryllium	X	---	X
Boron	X	---	X
Cadmium	X	---	X
Calcium	---	X	X
Chromium	X	X	X
Cobalt	---	X	X
Copper	X	---	X
Iron	---	X	X
Lead	X	---	---
Lithium	X	---	X
Potassium	---	X	X
Magnesium	---	X	X
Manganese	---	X	X
Mercury	X	---	---
Molybdenum	---	X	X
Nickel	X	---	X
Selenium	X	X	---
Sodium	---	X	X
Silicon	---	X	X
Silver	X	X	X
Strontium	---	X	X
Thorium	---	X	---
Tin	X	---	X
Titanium	---	X	X
Vanadium	---	X	X
Zinc	X	X	X

TABLE 7. ADDITIONAL METALS ANALYSIS USING NEUTRON ACTIVATION  
Untreated and Treated Ash (Solid)

<u>Metal</u>	<u>Neutron</u> <u>Activation Only</u>
Cesium	X
Dysprosium	X
Gallium	X
Hafnium	X
Indium	X
Rubidium	X
Scandium	X
Uranium	X

Twenty-one responses were received and evaluated. The responses were divided into 11 S/S processes, 6 vitrification processes and 4 other miscellaneous processes. Based upon the evaluation criteria, the S/S process proposals were judged to be superior. In order not to select similar S/S process types (e.g., two cement based) with the limited resources available, the decision was made to select the best proposal out of the different types available. The vitrification process proposals were generally incomplete and failed to address some major issues. This, in conjunction with the potential high quantities of residues required for most of these processes, resulted in the decision not to select one for evaluation. Alternatives for evaluating vitrification processes are being pursued. Proposals in the other miscellaneous category were not acceptable and were rejected.

During the request for participation, evaluation and selection process, provisions were made for maintaining confidentiality of information so marked by the responders.

Following is a brief description of each of the processes selected.

**Cement Based Process** - This process involves the addition of polymeric adsorbents to a slurry of MWC ash prior to the addition of portland cement. The final product is soil-like rather than monolithic.

**Silicate based process** - This is a patented process using soluble silicates as an additive with cement. The additives are used to promote several types of reactions with the polyvalent metal present to produce insoluble metal compounds, gel structures, and promote hydrolysis, hydration and neutralization reactions. The process immobilizes heavy metals through reactions involving complex silicates. The final product is clay-like material.

**CKD process** - This is a patented process involving mixing the MWC ashes with quality controlled waste pozzolans and water. Good quality control on the reagents is required because they are secondary materials derived from processing other materials. Therefore, the pozzolanic characteristics critical to the process are subject to change. The finished product is similar to moist soil, but hardens to a concrete-like mass within several days.

**Phosphate process** - A water soluble phosphate is used in this patented process to convert lead and cadmium to insoluble forms. The process is designed such that fly ash is mixed with lime, then this material can be mixed with the bottom ash and the mixture treated with a source of water soluble phosphate. The process does not alter the physical state of the ash.

#### DEMONSTRATIONS

**Process** - The procedures for conducting the demonstrations were established so that the process vendors could review data from characterizations of the various ash prior to the demonstration. Samples of the ashes were also furnished to the vendors so that they have the opportunity to pretest their process prior to the demonstration. This permitted them to make modifications if desired. Vendors were responsible for providing any specialized equipment or ingredients required. Each agreed to permit

observation by U.S. EPA selected observers if it was necessary to conduct the demonstration at the vendor's facilities. Otherwise the demonstrations were to be conducted at a U.S. EPA selected facility and observed by U.S. EPA designated staff.

During the process demonstration, each vendor was requested to carry out three replicate batches for each ash type. A total of between 50 and 100 gallons of each ash type is being treated for each process. Numerous molds and samples are prepared from these batches. All molds and sample containers are provided by WES and U.S. EPA. Each vendor provides enough process additives for analysis and archiving. Most equipment and laboratory facilities required for the demonstrations are provided by WES.

Scale - The processes are being demonstrated at bench scale. Reasons for this include the technologies being tested, resources required for full scale demonstrations and the desire to include as many different processes as possible within available resources. The program plan was to conduct a full scale field demonstration of a selected process if deemed necessary. Because of the nature of S/S technologies, U.S. EPA and the TAP believed that bench scale demonstrations were adequate to prove if the technology is an effective treatment for MWC residues. Sufficient experience is available for conducting the engineering and design required for scaling to a specific situation. Furthermore, the bench scale permitted much more detailed testing to be completed and thus more exploration of the basic mechanisms involved in the process. This in turn will assist in the determination of expected long-term behavior. A drawback with this scale however, is the difficulty in sampling and variability associated with bottom ashes.

Status - The S/S process demonstrations have been completed. Because of the nature of the S/S process, sample curing requirements (i.e., 28 days) and other specific test requirements, the physical testing, chemical testing and analytical procedures were delayed and just recently completed. The very large volume of data generated is still being compiled, organized and interpreted. The final report is expected by the end of June 1991.

Future MITE Demonstrations - Future MITE demonstration candidates have been solicited by notice in the Commerce Business Daily, through appropriate MSW trade organizations, interested developers and similar means. At this time, emphasis for these demonstrations is expected to be on processes for recovering marketable products from the MSW stream. Additional industry and state cooperative evaluations of MWC ash treatment and/or utilization processes are planned under separate programs.

## RESULTS

Complete results from the various physical and chemical tests are not available at this writing. Samples of the data and results being generated are provided in Tables 8 through 11.

Strengths after Water Immersion - One objective of conducting the leach testing and physical tests was to evaluate the effectiveness of the various processes to retain physical durability and the metals of concern when exposed to different stresses. One potentially valuable observation is how well the

physical structure can be expected to withstand degradation under exposure to wet conditions (e.g., marine environment, road base, construction blocks, etc). If one assumes that physical durability will improve the capability of the treated form to resist leaching, then strength before and after immersion will provide insight about this characteristic. Table 8 compares the unconfined compressive strength (UCS) before and after immersion in a water solution of the residues (i.e., bottom, air pollution control (APC), and combined) treated with the various processes.

Compared to the other processes, the control process (i.e., cement) showed somewhat better effectiveness in retaining physical strength after immersion. Also of interest is the general trend that the APC residues (as compared to bottom and combined) appeared to be more difficult to treat as measured by lower strengths. While this confirms observations from other researchers, one must note that UCS measurements results often have wide ranges. However, data presented in Table 8 had reasonable variations with exception of WES combined ash after 28 day cure time and the bottom ash after 28 day immersion.

In comparing strengths of solidified waste forms, one must note that there is little scientific evidence that directly relates increased strength with decreased release rates of pollutants of environmental concern. Also increased strength may not be important in the case of placement in a landfill. In such cases strength concerns deal with sufficient load bearing capacity necessary to support equipment and landfill covers, etc. In some cases, these may be as low as 12 to 15 psi or lower. These relatively low strengths often can be easily achieved through routine compaction. Additionally many MWC residues contain sufficient pozzolanic properties which when combined with the excess lime from wet scrubbers will result in some hardening of the ashes without additional additives<sup>9</sup>.

Strengths greater than those shown in Table 8 would be required for potential uses such as shore erosion control and some construction applications. Higher strengths have been routinely achieved<sup>10</sup>.

#### CONTAMINANT RELEASE AND COMPARISON OF LEACH TEST

One of the most critical concerns associated with management of MWC residues is the potential environmental damage from release of heavy metals such as lead and cadmium. Several leach tests (or extractions) were performed to help assess the expected release under different conditions. Tables 9, 10, and 11 summarize some preliminary results and provide examples of the types of comparison one might make when all the results are available. Table 9 compares the concentrations of constituents indicated in the leachates (extracts) when the WES control treated combined ash was subjected to the Toxicity Characteristics Leaching Procedure (TCLP) and the distilled water leach (DL) test. Also provided are the TCLP regulatory limits. Note in all cases, the concentrations of the TCLP regulatory metals of concern were below the regulatory limits. In the case of the distilled water leach test, barium leached at levels above the TCLP limit. The principal species leached using the distilled water leach test were Ca, K, Na, and Cl. Of interest to note is that the total dissolved solids (TDS) were approximately 2300 mg/l, significantly greater than the primary drinking water standard of 500 mg/l.

TABLE 8. COMPARISON OF UNCONFINED COMPRESSIVE STRENGTH (UCS) OF STABILIZED MWC RESIDUES (after 28 days of curing, and after 28 day immersion in water solution (0.10 g lime/L distilled water) subsequent to 28 days of curing. Curing was carried out at 20° C and 98 percent relative humidity)

Process	Bottom Ash UCS (psig)	APC Residue UCS (psig)	Combined Ash UCS (psig)
Untreated <sup>1</sup>			
28 day cure	7	5	10
28 day immersion after 28 day cure	CD <sup>2</sup>	CD	CD
WES Control			
28 day cure	1152	555	441 <sup>3</sup>
28 day immersion after 28 day cure	1075	434	531
Vendor 1			
28 day cure	1081	136	252
28 day immersion after 28 day cure	432 <sup>4</sup>	224 <sup>5</sup>	29
Vendor 2			
28 day cure	150	175	228
28 day immersion after 28 day cure	149	CD	152
Vendor 3			
28 day cure	350	154	275
28 day immersion after 28 day cure	CD	CD	18
Vendor 4			
28 day cure	55	unconsolidated <sup>6</sup>	83
28 day immersion after 28 day cure	197	unconsolidated	176

1 - Untreated MWC residue prepared at optimum moisture content and compacted with Modified Proctor Compaction Effort.

2 - CD - Cube Disintegrated - Cube disintegrated from free standing monolith to unconsolidated form.

3 - Wide variation in data (Coefficient of Variation = 0.54)

4 - Wide variation in data (Coefficient of Variation = 1.3)

5 - Cubes had spongy consistency after immersion.

6 - Unconsolidated - Following treatment product remained unconsolidated.

Table 9. COMPARISON OF LABORATORY EXTRACT CONCENTRATIONS FOR LEACHING TESTS ON TREATED MWC RESIDUES.

PROCESS: WES Control		ASH TYPE: Combined Ash		TCLP
	DL E(1+2)	DL E(3+4)	TCLP (E2)	REG. LIMIT
<b>Metals (ug/l)</b>				
Aluminum	4566.7	8600.0	9266.7	
Antimony	40.4 U	40.4 U	40.4 U	
Arsenic	10.0 U	10.0 U	13.0 B	50
Barium	2626.7	1200.0	500.0	1000
Beryllium	2.5	2.5	3.0	
Boron	NA	NA	NA	
Cadmium	1.0 U	1.0 U	620.0	1000
Calcium	226666.7	136666.7	196666.7	
Chromium	12.0 B	13.7	23.8	
Cobalt	11.3	7.0 U	60.7	
Copper	253.3	75.3	2890.0	
Iron	19.7	12.7	3066.7	
Lead	28.7	12.7	1333.3	5000
Lithium	56.7	15.3 B	66.7	
Magnesium	13.0	8.0	105666.7	
Manganese	3.7 U	3.7 U	7466.7	
Mercury	0.2 U	0.2 B	0.7 A	200
Molybdenum	63.0	43.0	18.3 B	
Nickel	20.0 U	20.0 U	293.3	
Potassium	136666.7	3200.0	66000.0	
Selenium	5.0 U	5.0 U	5.0 U	
Silicon	1900.0	1466.7	30666.7	
Silver	7.4 U	7.4 U	7.4 U	5000
Sodium	120000.0	2666.7	93333.3	
Strontium	2700.0	546.7	2366.7	
Tin	55.0 U	55.0 U	55.0 U	
Titanium	12.0 U	12.0 U	29.0 A	
Vanadium	10.8	8.9	7.4	
Zinc	36.0	37.3	30333.3	

U=undetected, A=U(1 of 3), B=U(2 of 3), NA= not analyzed

Table 9. COMPARISON OF LABORATORY EXTRACT CONCENTRATIONS FOR LEACHING TESTS ON TREATED MWC RESIDUES (continued).

PROCESS: WES Control		ASH TYPE: Combined Ash		
	DL E(1+2)	DL E(3+4)	TCLP (E2)	
<b>Anions (mg/l)</b>				
Bromide	13.43	1.34	NA	
Fluoride	NA	NA	NA	
Chloride	881.33	75.17	NA	
Sulfate	5.32	7.26	NA	
<b>Nitrogen Species:</b>				
Nitrite	NA	NA	NA	
Nitrate	3.61	1.13	NA	
Ammonia	NA	NA	NA	
Phosphorous	1.00 U	1.00 U	NA	
<b>Other Assays (mg/l)</b>				
pH	11.59	10.88	11.21	
TDS	2313.33	507.33	NA	
COD	58.60	15.60	NA	
TOC	23.90	3.83	NA	

U=undetected, A=U(1 of 3), B=U(2 of 3), NA= not analyzed

DL E(1+2)=distilled water leach test, extracts 1 and 2 combined for analysis

DL E(3+4)=distilled water leach test, extracts 3 and 4 combined for analysis

TCLP (E2)=TCLP leach test, extractant 2

TABLE 10. COMPARISON OF SPECIES RELEASE FOR LEACHING TESTS ON TREATED MWC RESIDUES (mg released/kg treated product, dry solid).

PROCESS: WES Control		ASH TYPE: Combined Ash			
	DL E(1..4)	TCLP (E2)	Avall.	Total (SW846)	Total (NAA)
<b>Metals (mg/kg ds)</b>					
Aluminum	286.6	205.7	4255.1	27054.3	49089.9
Antimony	1.8 U	0.9 U	8.9 B	NA	243.9
Arsenic	0.4 U	0.3 B	3.5	25.6	NA
Barium	83.1	11.1	155.0	750.1	NA
Beryllium	0.1	0.1	0.6	15.5	NA
Boron	NA	NA	NA	NA	NA
Cadmium	0.0 U	13.8	20.4	25.3	34.1
Calcium	7905.9	43840.3	103279.8	NA	142810.3
Chromium	0.6	0.5	4.8	84.7	465.8
Cobalt	0.4 U	1.3	3.5	NA	36.6
Copper	7.2	64.4	281.0	1107.1	1573.4
Iron	0.7	68.1	152.7	NA	92392.4
Lead	0.9	29.6	281.0	1263.9	NA
Lithium	1.6 B	1.5	3.8 A	11.5	NA
Magnesium	0.5	2354.0	3753.3	NA	NA
Manganese	0.2 U	166.2	302.6	NA	1609.9
Mercury	0.0 B	0.0 A	0.1	7.1	NA
Molybdenum	2.3	0.4 B	9.0	NA	NA
Nickel	0.9 U	6.5	13.7	114.5	NA
Potassium	3043.7	1471.3	4766.7	NA	NA
Selenium	0.2 U	0.1 U	1.1 U	5.4 U	0.8
Silicon	73.3	680.8	7203.8	NA	NA
Silver	0.3 U	0.2 U	1.6 U	2.3	6.8
Sodium	2669.6	2081.3	4405.5	NA	26315.5
Strontium	70.6	52.7	161.5	NA	NA
Tin	2.4 U	1.2 U	11.9 U	155.2	NA
Titanium	0.5 U	0.6 A	2.6 U	NA	5414.1
Vanadium	0.4	0.2	1.4 U	NA	41.7
Zinc	1.6	675.0	1750.8	3102.7	4830.7

U=undetected, A=U(1 of 3), B=U(2 of 3), NA= not analyzed

TABLE 10. COMPARISON OF SPECIES RELEASE FOR LEACHING TESTS ON TREATED MWC RESIDUES (mg released/kg treated product, dry solid) (continued).

PROCESS: WES Control

ASH TYPE: Combined Ash

	DL E(1..4)	TCLP (E2)	Avall.	Total (SW846)	Total (NAA)
<b>Anions (mg/kg ds)</b>					
Bromide	321.6	NA	3584.2 U	151.5	736.2
Fluoride	NA	NA	NA	NA	NA
Chloride	20814.0	NA	31619.7	15522.1	16543.6
Sulfate	274.2	NA	29620.8	125.2	NA
<b>Nitrogen Species:</b>					
Nitrite	NA	NA	NA	NA	NA
Nitrate	103.1	NA	NA	3.4	NA
Ammonia	NA	NA	NA	3.9	NA
Phosphorous	43.4 U	NA	215.3 U	0.1 A	NA
<b>Other Assays (mg/kg ds)</b>					
pH (S.U.)	11.59	11.21	4.00	11.6	NA
TDS	61382.66	NA	NA	23467.1	NA
COD	2371.13	NA	NA	41149.0	NA
TOC	603.51	NA	NA	6576.4	NA

U=undetected, A=U(1 of 3), B=U(2 of 3), NA= not analyzed

DL E(1..4)=distilled water leach test, extracts 1, 2, 3 and 4

TCLP (E2)=TCLP, extractant 2

Avall.=avallabililty leach test

Total (SW846)=total analysis as per USEPA methods SW-846

Total (NAA)=total analysis by neutron activation

TABLE 11. COMPARISON OF SPECIES RELEASE FOR UNTREATED AND TREATED RESIDUES CORRECTED FOR PROCESS DILUTION.

	PROCESS: WES Control		ASH TYPE: Combined Ash	
	TCLP Untreated	Treated	DL E(1..4) Untreated	Treated
<b>Metals (mg/kg ash, ds)</b>				
Aluminum	2091.2	246.8	2425.7	344.0
Antimony	0.6 A	1.1 U	1.0	2.1 U
Arsenic	0.3 A	0.3 B	0.1	0.5 U
Barium	19.9	13.3	38.2	99.7
Beryllium	0.0 U	0.1	0.0	0.1
Boron	34.0	NA	1.0	NA
Cadmium	11.1	16.6	0.0	0.1 U
Calcium	39589.1	52608.3	10676.3	9487.0
Chromium	1.5	0.6	0.3	0.7
Cobalt	2.3	1.6	0.2	0.5 U
Copper	62.6	77.3	12.9	8.6
Iron	715.9	81.7	1.2	0.8
Lead	47.3	35.6	0.2	1.1
Lithium	1.4	1.8	1.1	1.9 B
Magnesium	2038.7	2824.8	2.7	0.5
Manganese	208.2	199.4	0.1	0.2 U
Mercury	0.0	0.0 A	0.0	0.0 B
Molybdenum	0.3	0.5 B	0.9	2.8
Nickel	10.6	7.8	0.5	1.0 U
Potassium	2557.6	1765.6	4323.8	3652.4
Selenium	0.4 U	0.1 U	0.1	0.3 U
Silicon	725.4	817.0	14.7	87.9
Silver	0.1 U	0.2 U	0.1	0.4 U
Sodium	2792.8	2497.5	4463.1	3203.6
Strontium	60.5	63.2	70.7	84.8
Tin	0.4 U	1.5 U	0.7	2.9 U
Titanium	1.0	0.8 A	1.8	0.6 U
Vanadium	0.1 U	0.2	0.1	0.5
Zinc	858.2	810.0	1.1	1.9

U=undetected, A=U(1 of 3), B=U(2 of 3), NA= not analyzed

TABLE 11. COMPARISON OF SPECIES RELEASE FOR UNTREATED AND TREATED RESIDUES CORRECTED FOR PROCESS DILUTION (continued).

PROCESS: WES Control		ASH TYPE: Combined Ash		
	TCLP		DL E(1..4)	
	Untreated	Treated	Untreated	Treated
<b>Anions (mg/kg ash, ds)</b>				
Bromide	299.7	NA	305.2	385.9
Fluoride	7.6	NA	4.1	NA
Chloride	14705.1	NA	28511.5	24976.8
Sulfate	14759.7	NA	2153.6	329.0
<b>Nitrogen Species:</b>				
Nitrite	0.5	NA	0.7	NA
Nitrate	1748.4	NA	38.1	123.7
Ammonia	NA	NA	NA	NA
Phosphorous	26.5	NA	3.0	52.1 U
<b>Other Assays (mg/kg ash, ds)</b>				
pH (S.U.)	5.19	11.21	10.97	11.59
TDS	NA	NA	59900.0	73659.2
COD	NA	NA	2489.4	2845.4
TOC	NA	NA	648.3	724.2

U=undetected, A=U(1 of 3), B=U(2 of 3), NA= not analyzed

DL E(1..4)=distilled water leach test, extracts 1, 2, 3 and 4

TCLP (E2)=TCLP, extractant 2

Table 10 compares species release for several leaching tests and total concentrations as determined by SW 846 and Neutron Activation Analysis (NAA). Values indicated are based on dry weight of treated product. Several points of interest are:

- total analysis of species by SW 846 was poor relative to those determined by neutron activation. Compared to NAA, Method SW 846 recovered 55% of Al, 74% of Cd, 18% of Cr, 70% of Cu and 64% of Zn.

Following are observations of the relative amounts of the indicated species that leached using the indicated leach test when compared to either the NAA or SW 846 analysis:

- Using the availability leach test:
  - less than 1% of Ca, Fe and Ti leached,
  - between 1% and 5% of Sb, Be, and V leached,
  - between 5% and 10% of Al, Co, and Sn leached,
  - between 10% and 20% of As, Cu, Mn, Ni, and Na leached, and
  - greater than 20% of the following leached (actual numbers are indicated), Ba(21%), Cd(60%), Ca(72%), Pb(22%), Zi(33%), and Zn(36%).
- Using the TCLP:
  - less than 1% of Al, Be, Cr, Fe and V leached,
  - between 1% and 5% of As, Ba, Co, Cu, and Pb leached,
  - between 5% and 10% of Mn, Ni, and Na leached,
  - between 10% and 20% of Li and Zn leached, and
  - 40% of Cd and 31% of Ca leached.
- Using the distilled water leach test:
  - less than 1% of Al, As, Be, Cr, Co, Cu, Fe, Pb, Mn, Ni, V, and Zn leached,
  - between 5% and 10% of Ba, Ca, Li, and Na leached.

Compared to total analysis, Pb can be used as an example to compare to the TCLP, the distilled water and the availability tests as follows:

- Availability - 22% Pb leached
- TCLP - between 1% and 5% Pb leached

- distilled water - less than 1% leached

In the case of the available leach test results, note that the amounts of sulfate and chloride released were greater than the amounts present as indicated by the total analysis, indicating that these procedures may be poor for the species indicated. Also note that the total dissolved solids recovered were greater than total analysis indicated.

Species released by the TCLP and the DL test from untreated combined ash as compared to the WES treated ash is provided in Table 11. Values presented are corrected for dilution effects of the additive. For this particular case, treatment resulted in no significant change in the release of Ba, Ca, Cu, Pb, Li, Mg, Mn, Ni, K, Si, NA, Sr, Zn, Cd, and TDS. Treatment did reduce release of Fe, Al, and SO<sub>4</sub>.

### CONCLUSIONS

This paper presented preliminary results from evaluating several S/S processes for treating MWC residues. Conclusions must wait until all analysis and data interpretation are complete. Results presented, however, do indicate the potential value of the data and the comparison which will be facilitated when all results are available.

Preliminary data do indicate potential problems with relying on selected leach tests and analyses or relying on only one leach test for assessing effectiveness of treatments. Data presented also indicates the value of strength testing before and after immersion as a comparative tool to judge different processes. The use of strength, however, as a measure of effectiveness to reduce release of contaminants is not proven.

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WEATHERING OF SELECTED DEGRADABLE PLASTIC MATERIALS  
UNDER OUTDOOR AND LABORATORY EXPOSURE CONDITIONS

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ABSTRACT

Enhanced photodegradable plastic films show a faster loss in ultimate tensile elongation on exposure to the outdoor environment relative to a comparable regular plastic film. The acceleration factor obtained was 4-13 depending on the type of photodegradable polymer tested. The factor was markedly dependent upon location of exposure with Phoenix (Arizona) showing the fastest rate of breakdown of the five outdoor sites tested. This geographic variation appears to be mainly a result of varying amounts of sunlight received at the different locations.

A functional set of definitions and a classification of Enhanced Degradable Plastics has been developed.

This paper has been reviewed in accordance with the U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

Responding to a consistently high per capita consumption of plastics amounting to about 190 lbs/person,<sup>1</sup> the US chemical industry annually produces in excess of 50 billion pounds of plastic resin.<sup>2</sup> Of this, nearly a fourth is used by the packaging sector<sup>3</sup> to fabricate products which often have a very short useful lifetime (or are even single-use items). The familiar plastic bags, foam cups, fast food packages and drinking straws belong to the latter group of products and invariably are highly visible components of municipal solid waste as well as urban litter.

The litter problem usually associated with the urban areas, has in recent times turned out to be even more severe in the case of marine environment.<sup>4</sup> Since the industry-wide switch over from natural to synthetic gear in the 1940's,<sup>5</sup> the fishing industry has become the largest single user of plastics at sea. Accidental losses and dumping of gear-related plastics as well as packaging materials from fishing vessels is a major source of plastic pollution of the world's oceans. Discharge from merchant vessels and passenger liners further exacerbate the situation. Plastic debris at sea is not merely an aesthetic problem, but is also a serious ecological threat. A variety of marine animals including different types of sea birds, turtles, fish, marine mammals and cetaceans are reported to suffer from entanglement in or ingestion of plastic debris.<sup>6</sup> Recently observed decreases in population of seals, for instance, have been primarily linked to the effect of plastics debris in the oceans.<sup>7</sup>

Along with public education, the use of enhanced degradable plastics, often referred to as "degradable plastics", has been proposed as a corrective strategy.<sup>8</sup> Degradable plastics are those plastic materials chemically modified or otherwise formulated to deteriorate at an accelerated rate in the outdoor environment. The more rapid environmental deterioration of degradable plastics compared to regular plastics, is expected to drastically reduce the lifetimes of debris and thereby remove plastic waste from the environment at an observable rate outdoors. In view of the exceptional durability and extended lifetime of regular plastic debris, any small improvement in the rate of degradability will have a significant impact on the waste management.

### Degradable Plastics

The term "Degradable Plastics" is strictly a misnomer suggesting the existence of non-degradable plastics; all polymers are of course environmentally degradable. In the case of synthetic organic polymers, the rate of biologically mediated degradation in the environment is too slow to be of any practical consequence. It is more appropriate to use the term "enhanced degradable plastics" or "rapidly degradable plastics" for those plastics designed (or selected) for relatively faster breakdown in the environment.

Enhanced degradable plastics technology strives to accelerate the breakdown of commodity plastic materials by several different approaches; chemical modification of the polymer, synthesis of new rapidly biodegradable thermoplastics, and by the incorporation of additives into the plastic materials, to promote faster breakdown in the environment. There is no generally accepted level of enhancement in rate needed to classify a material as an enhanced degradable plastic. One such standard might be the naturally produced biopolymers which are presumably compatible with the environment. If a synthetic polymer approaches comparable rates of breakdown in the environment, it might be argued that the material also has a similar level of environmental acceptability.

Several different classes of such plastics have been developed over the years and these claim enhanced degradability in sunlight, under soil, in sea water (or marine mud), and under composting conditions. From a practical standpoint, use of Enhanced Degradable Plastics will have the following impact on solid waste management.

- (a) *Litter reduction.* The lifetime of litter will be reduced thus reducing the cost of litter collection and disposal. In this role, the enhanced degradable plastics might be regarded as being equivalent to source reduction if the lifetime of litter will be shortened to an extent to make collection unnecessary.
- (b) *Marine plastic waste.* Unlike with land litter, there is no mechanism by which plastic waste is removed from the marine/estuarine environments. In the absence of alternative strategies, the enhanced degradable plastics might play a role in addressing this need.
- (c) *Composting.* Mechanical sorting of the solid waste prior to composting is both costly and time consuming. If plastic films and containers can be left in the composting stream, it represents a substantial operational cost saving. Enhanced degradable plastics may therefore be desirable in a composting operation. The same is true of anaerobic digestion processes as well.
- (d) *Landfills and sewers.* These essentially anaerobic environments do not affect plastics. Consequently even natural products such as food wastes and yard wastes usually contained in plastic bags undergo very slow breakdown under dry landfill conditions. Containment of organic waste capable of ready degradation in enhanced degradable plastic bags might in some instances hasten their breakdown in a landfill.

The main goal of the present study was to assess the performance of selected common degradable plastics materials under several typical exposure conditions. Plastics were tested as films, and in the case of polystyrene as extruded foamed sheets, the forms in which these plastics occur in the post-consumer waste.

A major drawback in discussing enhanced degradable plastics is the lack of adequate definitions and a practical classification system. These are currently under development by the ASTM sub committee D20.96 and are expected to be available shortly. The following definitions apply to the present work.

**Disintegration:** The loss of integrity, embrittlement, or breakdown of a material on exposure to the environment.

**Deterioration:** Disintegration of a material predominantly due to physical changes. (e.g., damage to materials due to freeze-thaw cycles, damage from thermal expansion, dissolution, and damage from rodent and insect attack on plastics)

**Degradation:** Disintegration of a material primarily due to chemical processes. (light-induced degradation of polymers, hydrolysis, microbial assimilation of polymers.)

Note that degradation alters the chemical nature of the material while deterioration does not. The reader is cautioned that the above terms are used rather loosely, and in a widely different sense from above in the literature.<sup>9</sup> Both Deterioration and Degradation might be further classified according to the agency bringing about the disintegration. Table I illustrates the use of the

above terminology with the various types of breakdown. Examples of these processes and relevant enhanced degradable plastic products are shown.

Table I. Proposed Definitions of Environmental Breakdown Processes and Enhanced Degradable Plastics.

		Examples	Product
<p><b>DISINTEGRATION</b> Breakkdown (size reduction) of material into small fractions, including embrittlement</p>	<p><b>DEGRADATION</b> A disintegration caused predominantly by chemical changes</p>	<p><b>PHOTODEGRADATION</b> Light-Induced</p>	<p>a Ecolyte ECO resin</p>
		<p>b Plastigone</p>	
		<p><b>BIODEGRADATION</b> Brought about by living animals, plants, particularly microbes</p>	<p>c Biopol - ICI</p>
		<p><b>OXIDATIVE DEGRADATION</b> Caused by thermooxidative reactions</p>	<p>d --</p>
		<p><b>HYDROLYSIS</b> Caused by reaction with water</p>	<p>e --</p>
		<p><b>BIODETERIORATION</b> Brought about by living animals and plants</p>	<p>f ADM, Ecostar</p>
		<p><b>DISSOLUTION</b> (Hydrodeterioration) Brought about by water</p>	<p>g PCL/PE - Union Carbide Belland</p>
	<p><b>THERMAL DETERIORATION</b> Caused by freeze-thawing or thermal cycling forces</p>		

- a Polymers with ketone groups in main chain or as a side chain.
- b Metal-compounds additives for PE
- c Poly(hydroxybutyrate valerate)
- d Metal-compounds and inorganic pigments in polyolefins
- e Acid catalyzed hydrolysis of cellulose
- f Starch-polymer composites; biodegradable polymer - other polymer composite
- g Soluble acrylic copolymers; soluble poly(vinyl alcohol) files

## EXPERIMENTAL

### MATERIALS:

All plastic materials used in the study was obtained from the manufacturers as extrusion blown films. These were:

- |  |                                   |
|--|-----------------------------------|
| (a) Ethylene-carbon monoxide copolymer (~1% CO)<br>[ECO copolymer]                             | HiCone Division<br>ITW Company    |
| (b) LDPE film containing metal compound pro-oxidant<br>[LDPE/metal compound]                   | Plastigone Company                |
| (c) LDPE/starch granule blend, with metal compound pro-oxidant<br>[LDPE/starch/metal compound] | Archer Daniels<br>Midland Company |

Each manufacturer also submitted samples of plastic film not containing any degradable additive or not chemically modified to serve as a reference in the exposure experiment.

### EXPOSURE:

Results discussed here pertain to outdoor land and Weather-Ometer® exposures. Outdoor exposures were carried out according to ASTM D1435 with the samples exposed with a plywood backing at an angle of 45 degrees facing south. The following exposure locations were used.

- (a) Miami, FL
- (b) Cedar Knolls, NJ
- (c) Chicago IL
- (d) Wittmann, AZ
- (e) Seattle, WA

### ASSESSMENT OF DEGRADATION:

Tensile property determinations, particularly elongation at break, were used for assessing the extent of degradation of exposed plastic materials in the case of all samples except for foamed polystyrene. Tensile testing was carried out according to ASTM D882 standard method for plastic laminates.

The materials were also exposed in an Atlas Ci-65 Weather-Ometer® equipped with a borosilicate-filtered xenon lamp as the light source. The exposure was conducted in accordance with ASTM G26 and the cycle used was 102 minutes light/18 minutes light and water spray/63°C black panel temperature. This exposure cycle generally yields data which correlate well with Florida outdoor exposure.

## RESULTS AND DISCUSSION

The non-uniformity of outdoor exposure conditions is well known to lead to variability in weathering test results.<sup>10</sup> Unlike in the case of establishing permanence properties of regular plastic films, the outdoor exposure of enhanced degradable plastic films requires a much shorter period of exposure, often 2-3 weeks outdoors. As such, the short term (day to day) fluctuation

in key factors such as average temperature, rainfall, and the available sunshine, is likely to affect the variability of test data to a greater extent compared to longer exposures of months or years. In an attempt to overcome this difficulty a "duplicate exposure" protocol was developed during this work. This protocol, however, was used in selected exposure sites only due to cost constraints.

Figure 1 illustrates the basis of the "duplicate exposure" procedure. Essentially, each time a sample is removed from the original set of plastic films, it is replaced by a fresh sample. Thus, two complete sets of samples are available for testing at the end of the test period; one with 1,2,.....n<sup>th</sup> week of exposure and another with n<sup>th</sup>, (n-1)<sup>th</sup>, .....1<sup>st</sup> week of exposure. With no drastic changes in weathering conditions both sets should yield very similar data. Inconsistent data between the two sets would suggest non-uniform exposure conditions during the short duration of exposure.

SET 1	ADD	n	0	0	0	...	0	0	0
	REMOVE	0	1	1	1	...	1	1	1
	TOTAL	n	n-1	n-2	n-3	...	2	1	0
SET 2	ADD	1	1	1	1	...	1	1	0
	REMOVE	0	0	0	0	...	0	0	n-1
	TOTAL	1	2	3	4	...	n-3	n-2	n-1
EXPOSURE TIME		0	1	2	3	...	n-2	n-1	n
									Weeks

Figure 1. Double Exposure Protocol for an Exposure for  $n$  Weeks with Weekly Sampling of Set 1

Figure 2 shows typical data obtained for loss in tensile elongation at break due to outdoor exposure of ethylene-carbon monoxide (1%) copolymer. The shape of the curve suggests a logarithmic relationship between the elongation at break and duration of exposure. The enhanced degradable plastic material as well as the control material which is the same plastic without the degradable additive or modification show a similar dependence. However, in the case of the reference samples only minimal changes in elongation at break was obtained during the relatively short period of exposure and the data showed a high degree of scatter.

Kinetics of the change in tensile elongation at break can be conveniently studied by fitting the data with an empirical equation of the following form.

$$E = a + 10^{bd} \quad \text{where } E \text{ is elongation at break, } d \text{ is the duration of exposure and } a \text{ and } b \text{ are constants}$$

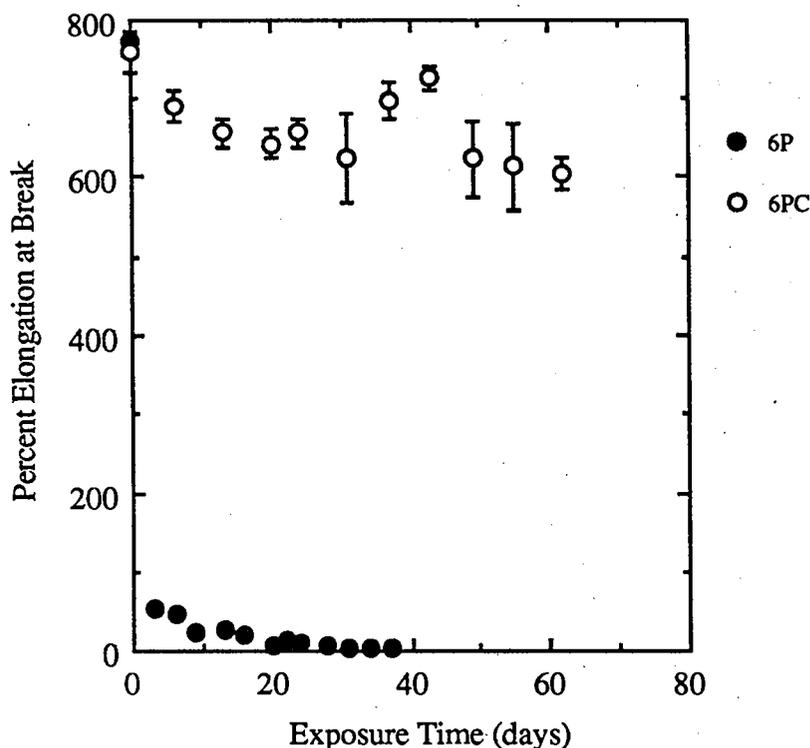


Figure 2. Percent elongation at break vs. exposure time for ethylene-carbon monoxide copolymer exposed outdoors in New Jersey. Code 6P refers to the copolymer samples, and 6PC refers to the low-density polyethylene control.

Plotting the data in the form suggested by the equation yields a pair of empirical parameters  $a$  and  $b$ . The parameter  $b$  is a measure of the rate of disintegration of the plastic films and a study of the change in value of  $b$  with geographic location can yield information as to variability that might be expected on the basis of climatic differences.

(a) *Agreement between "Duplicate Exposure" Sample Sets*

Figure 3 shows a typical set of data obtained for two sets of enhanced degradable samples exposed at a single location. The two sets of data agreed very well and a statistical analyses of the data showed them to belong to the same population with a high degree of confidence. This implies that the trend in data is not a result of sharp changes in key climatic factors (possibly available sunshine, and temperature) during the period of exposure.

While the scatter associated with data for enhanced degradable plastic materials at the different locations was minimal, that for the control plastic film often showed considerable scatter. The tensile elongation at break of regular polyethylene material did not change significantly due to degradation during the short duration of exposure monitored. However, some change due to "annealing" under exposure conditions leading to small changes in modulus, strength, and

ultimate elongation may often take place during initial stages of outdoor exposure. These lead to scatter in the data for control samples.

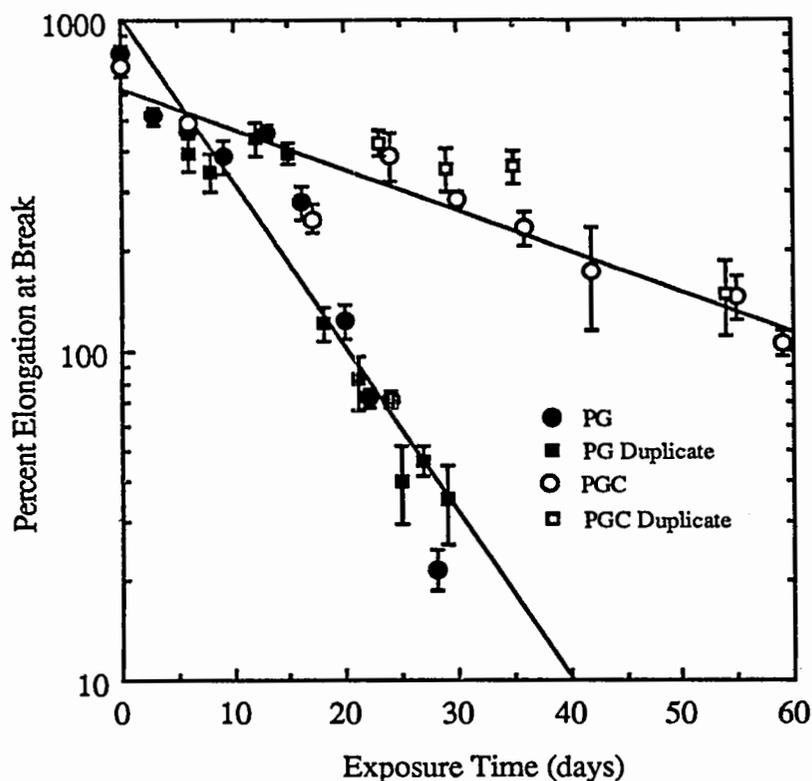


Figure 3. Percent elongation at break (log tensile elongation at break) vs. exposure time for LDPE films containing added metal compound pro-oxidant films exposed outdoors in Miami. Code PG refers to photodegradable polyethylene and PGC refers to LDPE control.

Table II lists the values of regression coefficients obtained for the "Duplicate Exposure" sample sets at various locations. The gradient of the line,  $b$ , which is an indicator of the rate of degradation agree well for the two sets of data at each location.

(b) *Geographic Variability*

A list of regression coefficients obtained for data on the three types of enhanced degradable plastics exposed at five outdoor locations is given in Table II. The data clearly indicate that the enhanced degradable plastics underwent a faster rate of environmental photodegradation compared to control plastic material. Ratio of the gradients for enhanced degradable and control polymer might be used as a measure of the enhancement in degradation (or an enhancement factor). As both the control and the enhanced-degradable samples were exposed concurrently at all locations, the enhancement factor would be expected to be constant. Average acceleration factors obtained at the different locations are shown in Table III.

TABLE II. Regression Coefficients for Fit of Test Data to Equation 1.

Sample	Location	$-bx10^3$ (days <sup>-1</sup> )	a	
1. LDPE Control	AZ	25	1047	
	IL	4	648	
	FL	14	953	
	NJ	10	708	
	WA	4	823	
	HiCone photodegradable six-pack ring material	AZ	257	550
		IL	87	246
		FL	65	184
		NJ	52	139
		WA	40	97
2. LDPE Film Control	AZ	33	607	
	IL	13	742	
	FL	22	917	
	NJ	12	139	
	WA	16	97	
	Plastigone material (LDPE/MX*)	AZ	122	885
		IL	49	1091
		FL	72	960
		NJ	50	1033
		WA	54	1004
3. Starch-polyethylene blends LDPE Film Control	AZ	25	300	
	IL	11	354	
	FL	9	371	
	NJ	6	340	
	WA	10	395	
	ADM, photodegradable starch/LDPE blends (LDPE/starch/MX)	AZ	391	89
		IL	148	67
		FL	129	41
		NJ	137	66
		WA	102	54

Note: MX = transition metal compounds (pro-oxidant additive).

TABLE III: Enhancement Factors for Three Types of Enhanced Degradable Materials for Different Geographic Locations.

Location	Enhancement Factors		
	ECO Copolymer	LDPE/MX*	LDPE/Starch/MX*
AZ	10	4	16
IL	22	4	14
FL	4	3	14
NJ	5	4	23
WA	10	3	10
Average (with standard error)	10 ± 3	4 ± 0.2	13 ± 2

\*MX = transition metal compounds (pro-oxidant additive).

ECO copolymer and the polyethylene/starch blends containing metal compounds showed about the same degree of enhancement, approximately by an order of magnitude. LDPE/MX material, somewhat similar to the latter plastic material in that it too contains metal compound pro-oxidants, showed a consistent factor of 4 for all locations of exposure.

It is of interest to compare the rankings of different geographic locations on the basis of the *b* parameter. Such a ranking might be made for both the control plastic films as well as for the enhanced degradable samples. However, the usefulness of the former is somewhat limited due to the considerable scatter associated with the data. Rankings obtained with the three types of enhanced degradable plastic films are as follows.

ECO copolymer	AZ > IL > FL > NJ > WA
LDPE/MX	AZ > FL > WA > NJ > IL
LDPE/starch/MX	AZ > IL > NJ > FL > WA

Except with the LDPE/metal compound pro-oxidant system (Plastigone material), the ranking for the control polyolefin did not agree with that for the enhanced degradable material. The difference in the above rankings is not surprising as the materials tested are able to undergo both photodegradation as well as thermal oxidative degradations. These processes may have different activation energies and the different climatic conditions at the test sites would have affected the rates of two degradation processes differently. The relevant activation energies are not reliably known for the three systems.

Assuming that the primary mechanism of degradation involved in outdoor exposure is photodegradation, it is reasonable to expect at least an approximate correlation between the rate of degradation with average available sunlight. The available light at different exposure locations varied widely. However, the spectral quality of sunlight at the five locations was also different depending upon the solar zenith angle and the season of the year. Any difference in the spectral irradiance distribution of sunlight will, of course, have a very significant impact upon the efficiency of degradation, its magnitude being determined by the activation spectrum for the particular polymer. A plot of the value of *b* parameter versus the average available sunlight for three types of degradable plastics is shown in Figure 4.

Surprisingly good correlations are obtained with the three exposure locations. The LDPE/starch/metal compound pro-oxidant system (ADM material) shows the highest degree of sensitivity (i.e. dependence of the rate of loss in extensibility on outdoor exposure upon the average amount of sunlight available at that location). However, the sensitivity of the plastic material to light-induced degradation is a function of formulation. By alternating the concentration of chromophores or the concentration of the pro-oxidant, the sensitivity of any of the tested films could be varied.

Weather-Ometer<sup>®</sup> exposure data were available for two types of enhanced degradable plastics only - six-pack ring material and Plastigone material. The loss of tensile elongation obtained in the Weather-Ometer<sup>®</sup> exposures were faster compared to the outdoor exposures. The relevant regression coefficients are shown in Table IV.

The acceleration factor obtained for Plastigone material is about 7 for Weather-Ometer<sup>®</sup> exposure. In the case of six-pack ring materials, the control sample was of different thickness; the acceleration factor, however, was about 3. Both are different from the average values obtained on the basis of the outdoor exposures. This is to be expected because of the widely different exposure conditions used. The Weather-Ometer<sup>®</sup> exposure involves continuous exposure

to light at a temperature much higher than the ambient. Temperature dependence of the photodegradation in the case of six-pack ring material and the contribution of thermooxidative degradation in the case of the Plastigone material can modify the results in such an accelerated study. However, the Weather-Ometer<sup>®</sup> exposure is an accelerated exposure compared to outdoor weathering as the b values (expressed in Table IV) in hours<sup>-1</sup> are much higher than those for outdoor exposure.

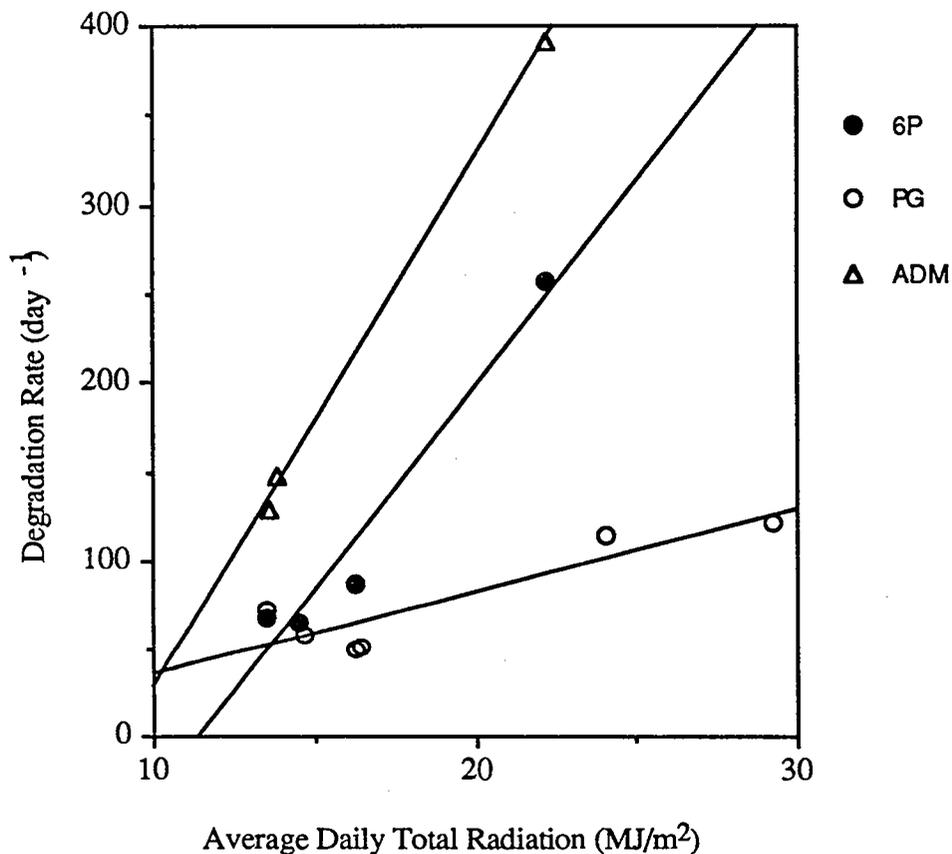


Figure 4. Rate of outdoor degradation versus the total global solar radiation for three types of Enhanced Photodegradable Plastics. 6P: ethylene-carbon monoxide copolymer (~ 1 percent CO), PG: LDPE containing added metal-compound pro-oxidants, and ADM: LDPE/starch (~6%) blends containing added metal compound pro-oxidants.

TABLE IV. Data from Weather-Ometer® Exposure of Enhanced Degradable Plastics.

Material	a	-b x 10 <sup>3</sup> (hrs <sup>-1</sup> )
Six-pack ring material	235	8.74
Control LDPE film	1463	2.59
Plastigone material	927	6.35
Plastigone control	599	0.94

### CONCLUSION

The three types of enhanced photodegradable plastic film samples tested showed the tensile elongation to be a property suitable for assessing the outdoor weathering rates for this class of plastics. This is a useful conclusion as the ASTM D20.96 committee on Degradable Plastics is considering the use of this test.

Plastic materials showed considerable amount of location-dependent variation in performance as measured by the rate of loss of ultimate elongation exposure. Arizona was the harshest outdoor exposure environment while New Jersey and/or Washington states were the mildest sites. The ratio of the breakdown rate of enhanced degradable materials relative to that of the base (unmodified) plastic, is considered as an enhancement factor. This factor shows variability from location to location. The location-dependent variability in enhancement factor can be explained in terms of different average sunlight levels available at these locations.

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## POLLUTION PREVENTION RESEARCH WITHIN THE FEDERAL COMMUNITY

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### ABSTRACT

One of the primary ongoing programs for promotion and encouragement of pollution prevention research is a cooperative program between the United States Environmental Protection Agency (EPA) and the Federal community at large. EPA's Waste Reduction Evaluations at Federal Sites (WREAFS) Program supports pollution prevention research through joint assessments of problematic areas at selected sites. The three primary objectives of the WREAFS Program are to: 1) conduct waste minimization assessments and case studies; 2) conduct research and demonstration projects jointly with other Federal activities; and 3) provide technology and information transfer of pollution prevention results.

This paper describes the WREAFS Program support of pollution prevention research throughout the Federal community and provides current status on all projects to date. These include joint efforts with the Departments of Agriculture, Defense, Energy, Interior, Transportation, Treasury, and Veteran Affairs. Seven of eleven projects are with the Department of Defense under the Branches of the Air Force, Army and Navy. Two projects are with the Coast Guard under the Department of Transportation. At present there are six waste minimization opportunity assessments (WMOA) in various stages of completion, four on-going and two recently initiated projects. Under the WREAFS cooperative umbrella, two other research and development projects are ongoing within the Departments of Agriculture and Defense.

These assessments have identified case study and research opportunities to implement pollution prevention for a range of military and industrial operations including metal cleaning, solvent degreasing, spray painting, vehicle and battery repair, ship bilge cleaning, torpedo overhaul, buoy restoration, lens grinding, hospital operations and other industrial processes.

The waste minimization recommendations are source reduction methods including technology, process and procedural changes and recycling methods of reuse or recycling. The WMOA consists of four steps: Planning and Organization, Assessment, Feasibility Analysis, and Implementation. The fourth step, implementation, is conducted at the discretion of the Federal facility.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

The objectives of the WREAFS Program are to identify new technologies and techniques for reducing wastes from industrial processes used by Federal agencies and to enhance the adoption of pollution prevention through technology transfer. New techniques and technologies for reducing waste generation are identified through waste minimization opportunity assessments and are evaluated through joint research, development and demonstration (RD&D) projects. The information and data from these projects are then provided to both the public and private sectors through various technology transfer mechanisms, including project reports, project summaries, conference presentations and workshops.

The waste minimization opportunity assessments are conducted by an assessment team that is composed of personnel from EPA, staff from the federal facility that is cooperating in the program and others who can provide technology and processing expertise. The assessments follow the procedures described in the EPA Report, Waste Minimization Opportunity Assessment Manual<sup>1</sup> (EPA/625/7-88/003)<sup>1</sup>. This manual provides a systematic procedure for identifying ways to reduce or eliminate waste generation. The development of this procedure was supported by the Risk Reduction Engineering Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio.

As a result of joint waste minimization opportunity assessments (WMOA's), RD&D projects are identified with recommendations for pollution prevention under the implementation phase. The demonstration projects are conducted under interagency agreements with joint funding by EPA and the cooperating Federal agency. Waste minimization workshops and other technology transfer methods are used to communicate the results of these projects to the Federal community and the private sector.

## WREAFS PROGRAM PROCEDURES

The WREAFS Program procedures used for conducting the waste minimization assessments are closely related to the WM procedures presented in the Manual. Figure 1 describes the course followed by a typical WREAFS project. The assessments consist of four major phases:

- (1) Planning and Organization: organization and goal setting;
- (2) Assessment: careful review of a facility's operations and wastestreams and the identification and screening of potential options to reduce waste;
- (3) Feasibility Analysis: evaluation of the technical and economic feasibility of the options selected and subsequent ranking of options;
- (4) Implementation: procurement, installation, implementation and evaluation.

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<sup>1</sup> Waste Minimization Opportunity Assessment Manual (EPA/625/7-88/003) is available free from CERL, Cincinnati.

Many of the WM opportunities identified during WREAFS projects involve low-cost changes to equipment and procedures presently employed at other Federal facilities or within private industry. These WM opportunities can often be implemented by the facility without extensive engineering evaluations. Some other WM opportunities identified during these projects will require further study before full implementation can be realized. Typically, opportunities requiring further evaluation are those that have the potential for affecting the process and/or require the use of new procedures or equipment. In such cases it may be necessary to conduct demonstration projects.

## DEMONSTRATION AND EVALUATION PROJECTS

The types of research projects that can be pursued under the WREAFS Program are those that are expected to advance the knowledge and practice of waste minimization technologies and methods, and have broad applicability to Federal facilities and private industry. Depending on the nature and state of development of the WM option selected for demonstration and evaluation, these projects may include: (1) process design, (2) detailed design and specification, (3) system procurement, (4) installation and start-up, (5) monitoring and (6) reporting. Some projects may require bench-scale and/or pilot testing prior to or as a part of the demonstration project. Other projects may utilize full-scale equipment directly on the production line.

### COMPLETED ASSESSMENTS (WMOA'S)

Five WREAFS assessments are now completed, three at DOD facilities, including two with the Navy and one with the Army; one at the Veteran's Medical Center in Cincinnati, Ohio; and one with the Coast Guard at Governor's Island, New York. With these five, the assessment surveys have been completed and waste minimization options have been identified for implementation. A description of each project follows.

#### PHILADELPHIA NAVAL SHIPYARD

This project was conducted in cooperation with the Environment, Safety and Health Office of the Philadelphia Naval Shipyard (PNSY). The shipyard has an ongoing program for waste minimization. With their guidance, several industrial operations were selected for application of the new waste minimization procedures. The shipyard plans to use these results as guidance for evaluating other pollution prevention/waste minimization activities.

#### FACILITY DESCRIPTION

The Philadelphia Naval Shipyard, the nation's oldest continuously operating naval shipyard, is located in South Philadelphia on 1,000 acres of land. Since its inception, 127 ships have been constructed, with last ship launched in 1971. It now specializes in revitalizing and repairing ships already in fleet. The Service Life Extension Program (SLEP) is the shipyard's largest program and its comprehensive keel-up restoration and modernization overhaul extend the life of aircraft carriers by half, at approximately one-third of the cost of a new carrier.

## AREAS OF WM OPPORTUNITY EVALUATIONS

The industrial activities selected for this project included:

- Aluminum cleaning and spray painting

The aluminum cleaning is performed to remove oil and other materials from the surfaces of aluminum sheets prior to welding and is critical to the welding if not properly cleaned. The cleaning line consists of two process and two rinse tanks. The tanks become diluted and contaminated with waste liquids and are disposed. Spray painting involves solvent degreasing and a water curtain booth for painting. Paint solids from overspray and sludge residues are removed and drummed with booth water discharged into the sewer. For the discharge, one organic polymer is used for colloidal precipitant dispersion and a second for coagulation into a sludge for screen removal.

- Spray painting of steel parts including structural columns

Spray painting of steel parts requires an area for shot blasting and painting. A dry air filtration system, a booth for blasting and painting steel columns and a water curtain booth are required. All are used for epoxy spray painting of steel surfaces.

- Citric acid bilge derusting operations in drydock

This is a chemical cleaning process for ships' tanks, bilges and void spaces performed in drydock. It employs the use of a citric acid/triethanolamine (TEA) solution to remove oxides from metal surfaces with subsequent neutralization followed by rinsing. The volume of spent solutions from a derusting/neutralization/rinse operation is typically about 3000 gallons. It generally has a pH below 4.0, contains toxic metals and is hauled to a treatment/disposal facility.

## WASTE MINIMIZATION OPTIONS AND RECOMMENDATIONS

After the assessment and feasibility analysis phases were completed, seven options were evaluated and ranked. The best options for implementation were:

- Awareness and Training for personnel/procedure-related options

Paint and paint wastes comprise the second largest hazardous waste stream generated at the shipyard. A program emphasizing operator involvement and responsibility could reduce waste paint in overspray, paint remaining unused in cans and paint solidification prior to use.

- Dragout Reduction and Bath Maintenance and ● Two Stage Rinsing

A hand-held spray rinse applied over process tanks would return 90% of the dragout back to the process tank. A bath maintenance system employing an oil skimmer for floating oil/grease removal and a cartridge filter for suspended solids removal would extend the usable life of process tanks from 3 months to a year. Employing a two stage rinse with sequencing of first and second would prolong the life of the rinsing tanks.

## RESEARCH, DEVELOPMENT AND DEMONSTRATION

Recovery of concentrated citric acid solution represents a viable candidate for further research, development and demonstration. It would involve the implementation of equipment for the recovery of the citric acid/TEA solution. This process would employ an electro dialytic membrane unit for separation and removal of dissolved metals. This technology has been applied to similar chemical solutions but its application to this waste has not been previously demonstrated.

### FORT RILEY, KANSAS

This project is an assessment conducted at the U.S. Army Forces Command (FORSCOM) maintenance facilities at Fort Riley, Kansas. It was initiated from data received from the Fort Riley Environmental Office on amounts of hazardous waste streams generated onsite. There are ten other U.S. Army FORSCOM installations providing potential for application of similar waste minimization options.

### FACILITY DESCRIPTION

Fort Riley is a permanent U.S. Army Forces Command (FORSCOM) installation that provides support and training facilities for the 1st Infantry Division (Mechanized), Non-Divisional Units, and tenant activities. It is owned and operated by the U.S. Government and occupies approximately 121,000 acres in north central Kansas. Fort Riley provides the U.S. Army with the capability to house and train an Army division and associated land combat forces, as well as to service Army functions in the midwest area.

### AREAS OF WM OPPORTUNITY EVALUATIONS

Large hazardous waste streams are generated here consisting of spent automotive cleaning solvents and various RCRA listed wastes including waste battery acid, waste caustic cleaners and spent parts wash water. Currently these hazardous wastes are handled as follows:

- Waste battery acid collected in 15-gallon plastic drums
- Caustic cleaners collected in 55-gallon metal drums

Both are classified wastes and sent by truck to the hazardous waste storage facility

- Waste water from the automotive parts washer is discharged to an onsite nonhazardous waste evaporation pond system. These will eventually be reclassified under RCRA regulations as D002 and D008 waste due to alkalinity and lead content, respectively.

The areas selected for evaluations were the battery repair and service shop which generates waste battery acid, the automotive subassembly rebuild area that generates waste automotive wash water and the radiator repair shop where spent caustic cleaner is disposed as a hazardous waste.

### Battery Repair Shop

The battery service area drains about 7,200 gallons per year of battery acid for disposal. The drained batteries are inverted, and either disposed if determined unusable, or repaired and refilled with fresh 37 percent sulfuric acid, recharged and reused.

### Automotive Subassembly Rebuild Shop

Prior to rebuilding various automotive subassemblies, e.g., engines, clutches, transmissions, these units are disassembled and placed in a specially designed high pressure hot-water washer for cleaning. This washer continuously circulates hot alkaline solution through high-pressure jets to provide the cleaning action. The washer wastewater contains chromium and lead which must be disposed of as a RCRA characteristic waste.

## WASTE MINIMIZATION OPTIONS AND RECOMMENDATIONS

After the assessment phase the following recycling options were recommended for the two major wastes, waste battery acid and the washer wastewater.

### Recycling of Waste Battery Acid

After collection, the waste battery acid would be transferred to an acid-resistant tank and mixed by recirculating pumps. Based on specific gravity the acid strength would be adjusted to 37-38%  $H_2SO_4$  with 78% sulfuric acid to yield standard battery acid. This refortified acid would be pumped through an acid-resistant filter to remove particulates and collected in drums for use in the battery repair operation. Other treatment operations would be required for more extended battery life. The installation of an expensive acid-resistant cooler can be avoided with the use of 78% sulfuric acid (60° Baume) rather than 93-98% (66° Baume) due to heat evolved during mixing.

### Recirculation of Washer Wastewater

Instead of disposing of this wastewater as a hazardous waste, it would be recycled following filtration through an in-line filter to remove discrete particulates, followed by de-emulsification and removal of oils. Additional detergent would be added as needed and water recycled to the parts washer.

Implementation of recycling both the battery acid and the waste water would cost about \$35,000 with an annual operating cost savings of about \$149,000. Payback period for simultaneous implementation of options would be less than five months. Adequate testing of refortified, recycled battery acid and monitoring of the detergency of the washer wastewater would be required.

## RESEARCH, DEVELOPMENT AND DEMONSTRATION

Proposed particulate filtration and de-emulsification processes would qualify as research, development and demonstration projects. In-plant experimentation of filter element types, necessity for multiple filters and cleansing effectiveness of recycled wash water would require further determination.

## NAVAL UNDERSEA WARFARE ENGINEERING STATION KEYPORT, WASHINGTON

The purpose of this project was to identify waste minimization opportunities for two industrial units at the Naval Undersea Warfare Engineering Station (NUWES) in Keyport, Washington. This project was conducted in cooperation with the Naval Energy and Environmental Support Activity (NEESA) of Port Hueneme, California, in coordination with the Environmental Division (Code 075) of the NUWES Keyport Civil Engineering Department. Several departments at NUWES Keyport are involved in an ongoing program to further the process of waste minimization at NUWES.

### FACILITY DESCRIPTION

NUWES Keyport is located within the central Puget Sound area of northwestern Washington State. The Keyport property was acquired by the Navy in 1913 and first used as a quiet water range for torpedo testing. Later the Station was used for torpedo repair. The facility acquired its current name in 1978 in recognition of the inclusion of various undersea warfare weapons and systems engineering and development activities.

### AREAS OF WM OPPORTUNITY EVALUATIONS

The principal activities currently conducted at NUWES Keyport are the design and testing of torpedoes. These activities generate a variety of potentially hazardous wastes, including fuel, oil, hydraulic fluid and grease, various metal and plating bath liquids, paint and thinner, Freon®, alcohol, mineral spirits and other solvents, resins, acids and caustics, chromate and cyanide salts, pesticide residues, wastewater treatment sludge, waste dye and detergent.

The major component of waste management involves the use of Otto Fuel II (Otto fuel) which is used for propelling torpedoes. Otto fuel is composed of propylene glycol dinitrate with lesser amounts of 2-nitrodiphenyl-amine and di-n-butylsebacate. Otto fuel is a monopropellant in that it burns without oxygen. The Navy currently treats all Otto fuel-contaminated solid waste as an explosive, reactive waste. Two grades of usable Otto fuel are distinguished:

- Condition-A            pure, virgin Otto fuel used for torpedoes in fleet
- Condition-B            collected from defueled torpedoes and reused for proofing (testing) purposes.

The two areas selected by the Navy for evaluation were torpedo maintenance shops, both having similar operations, processes, and waste streams. The major activities of these two shops are as follows:

- Weapons Depot Maintenance of unproofed torpedos, i.e. ones that have exceeded shelf life of 8 years. The Otto fuel is drained and the torpedoes are disassembled and restored. In-water testing of torpedoes with subsequent breakdown and restoration.
- Advanced Capability tests the newest version of Mark 48 torpedo, assembling and proofing, disassembling, cleaning and reassembling.

- Research & Development assemble, proof, tear down, clean and reassemble torpedoes.
- Mark 46 Shop defuels, disassembles, cleans, reassembles and refuels Mark 46 torpedoes. Diethylene glycol (DEG) is used to clean fuel tanks after draining.

Wastes generated during these processes include:

- cyanide-containing liquid wastes and sludges that are Otto fuel combustion byproducts
- Otto fuel-contaminated solvents and oils generated during cleaning of parts
- Otto fuel-contaminated wastewaters
- Otto fuel-contaminated solids, primarily clothing and rags
- Used oil
- Used hydraulic fluid
- DEG (diethylene glycol) and Otto fuel contaminated rinse waters

The Otto fuel sump is an underground stainless steel holding tank for Condition-B torpedo fuel contaminated with seawater, fresh water and alcohol. A cyanide sump is located within the Otto fuel sump and contains sludges and wastes contaminated with cyanide as well as detergents, oils, grease and alcohol. Fuel is recovered from these tanks by separation and treatment.

All the wastestreams are RCRA reactive wastes.

## WASTE MINIMIZATION OPTIONS AND RECOMMENDATIONS

NUWES Keyport has performed well in the handling, storage and minimization of waste materials on-base. During this assessment, no major waste minimization options were identified that NUWES has not already implemented or plans to implement. However, the following five options were identified to aid in the process:

- Volume Reduction of Otto Fuel-Contaminated Clothing

This includes a) segregating used clothing and b) removing uncontaminated portions. This would significantly reduce the amount that needs to be disposed as a hazardous waste. Otto fuel has a distinctive yellow color that would facilitate recognition of contaminated clothing. Often only small areas are involved and these would be removed by cutting off the contaminated portions or by substituting disposal sleeves and leg cuffs. All other uncontaminated parts would be discarded as non-hazardous materials. This would require a minimal capital outlay and savings would be realized in reduced disposal costs.

- Automated Cleaning of Parts and Fuel Tanks

Automated cleaning of parts and fuel tanks would result in more efficient and faster cleaning, smaller amounts of hazardous waste liquids and smaller amounts of contaminated clothing. Three dip tanks were to be replaced soon with automatic parts washers using biodegradable cleaning liquids. More extensive or complete automation of cleaning operations within the two shops would aid in reducing wastes and would involve a cleaning media of water and detergent in an agitator or jet system or an ultrasonic cleaner. While this option would require capital outlay for the purchase

of a cleaning unit, it would allow for reduced disposal of cleaning solutions and reduced raw materials purchased. Payback period for this option is 0.4 years and is one of the two fastest payback periods (total capital investment/net operating cost savings) represented by these recommendations.

● Automated Fuel Tank Draining

Automated fuel tank disassembly by robotics has been in use at the Mark 46 Shop for 3½ years, resulting in more efficient and faster operations and smaller amounts of waste liquids and contaminated clothing. Similar equipment would be installed in the Mark 48 Shop and would have a relatively short payback period due to decreased costs of labor, contaminated clothing disposal and spill cleanup. The decreased demand on manpower could be refocused and utilized in other areas.

● Modify the Deep Sink Draining Schedule

Switching from automatic weekly draining to an "as needed" non-automatic schedule would result in reduced cost due to a smaller purchasing volume of cleaning solvents, reduced volume of hazardous waste disposal and less man-hours. This is the other option with the fastest payback period, only requiring schedule modification and no capital outlay.

● Recycling of Mineral Spirits

Mineral spirits used for the cleaning of parts are currently treated as a RCRA hazardous waste, combined with other liquid waste streams and sent to an official off-site facility for incineration. Recycling of the mineral spirits could be used to recover up to 86% of the spent solvent. This also has a short payback period, involving moderate to high capital outlay for equipment, but savings in both the decrease of disposal costs and purchase of mineral spirits, making it an appealing option.

## RESEARCH, DEVELOPMENT AND DEMONSTRATION

The following five research needs were identified during the course of this assessment:

- Evaluate cost effectiveness of clothing with disposable sleeves and cuffs.
- Develop a test for determination of spent deep sink cleaning liquids.
- Evaluate the cost feasibility of robotics for draining, defueling and rinsing torpedoes.
- Identify potential recycling options for waste hydraulic fluid.
- Evaluate current practices for used torpedo engine oil.

## U.S. COAST GUARD SUPPORT CENTER NEW YORK GOVERNORS ISLAND, NEW YORK

This project was conducted at U.S. Coast Guard facilities on Governors Island, New York in cooperation with Coast Guard officials. It was initiated through contacts with the Hazardous Waste Office in the Industrial Division and conducted through them with interviews of Coast Guard Headquarters officials in Washington. This project attempted to develop both management initiatives as well as technical changes that can be made at Governors Island for waste minimization purposes. Technical waste minimization evaluations conducted at this site centered on paint removal by blasting, painting and solvent recovery.

### FACILITY DESCRIPTION

Governors Island is located off the southern tip of Manhattan and is accessible primarily by a Coast Guard operated ferry. The island encompasses 175 acres and consists solely of Coast Guard facilities which are grouped together under the name "Support Center New York". The island serves as a support center for Coast Guard activities conducted within the New York area, for tenant commands located on the island and is the home port for a number of Coast Guard cutters. There are 22 different commands represented on the island, each of which reports to Headquarters in Washington or to an off-site location. Support Center New York supports all activities on the island, however it does not have authority over all commands.

### AREAS OF WM OPPORTUNITY EVALUATIONS

#### Management Activities

During the early stages of the assessment it was determined that a review of the hazardous waste management activities on Governors Island was a useful study area. Three areas were reviewed:

- *Successful waste minimization* steps currently in practice include use of lead-free paint throughout the Coast Guard, development of a new paint with lower volatile organic compound (VOC) content, use of solar batteries in aids-to-navigation requiring battery power and elimination of engine coolants containing dichromate additives. A hazardous waste compactor for paint cans has been purchased for decreasing volume of waste. Blasting grit used for paint removal has been reduced 50% by installation of a new baghouse and recycling system. Disposable brushes usage reduces the waste from brush cleaning thinner.

- *Waste minimization problem areas* identified included governmental issues concerning lack of motivation for compliance, funding and procurement practices. End-of-year spending results in purchase of new paint when current reserves are sufficient. Lack of proper storage for preservation of paint quality contributes to excessive waste. Turnover of military personnel contributes to problems of hazardous waste handling.

- *Site organization and facilities* are major contributing factors in the problems of waste generation and disposal. The presence of tenant commands with no centralized procurement nor accountability causes poor management of supplies. Use of multiple disposal contractors by tenant commands causes significant hazardous waste generation, primarily of paint. Storage facilities

throughout the island are unheated and promote degradation of paints resulting in large quantities for disposal. It has been estimated that 50% of paint disposal is unnecessary.

● *Potential solutions for problems* are recommended; starting with cultural changes emphasizing commitment on all levels, forceful expression of policies, employee training and incentive awards and conducting detailed engineering evaluations of the waste generating processes. This would require a concerted effort from both Coast Guard Headquarters in Washington and Support Center New York for policy changes, funding, implementation and technology transfer. Additional recommendations include addressing storage areas and procurement practices. Central warehousing could eliminate loss of paint from unheated lockers. A centralized purchasing system would eliminate duplication of supplies with short shelf life. Individual commands need to be more cognizant of waste generating potential. Accountability would be conducive to better waste minimization practices.

#### Technical Evaluation for Waste Minimization

Several technological operations and processes were identified as key areas for consideration of waste minimization opportunities. These included the following areas with suggested recommendations:

Maintenance of buoys used as navigational aids is one the Coast Guard's responsibilities. Buoys require refurbishing every 4-6 years. Old and degraded paint is removed by blasting with steel shot and several coats of durable paint are reapplied. Frequent painting is the means to preserve the appearance and protect the integrity of equipment exposed to aggressive saltwater environment.

Currently items are moved into a large blasting room and paint, biological growth and rust are removed by application of steel shot with a high pressure air gun. The steel shot is recycled , approximately five times, until it becomes too fragmented for use. Spent shot is collected, stored and disposed as a hazardous waste because of low levels of lead. Estimated cost for purchase and disposal of the shot approximates \$38,000 annually.

Equipment is spray painted using a Binks Airless 1 spraygun and a high pressure air system. Buoys are spray painted with several different paints, including an epoxy anti-foulant with a total of approximately 5,300 gallons of various coatings used annually. It is estimated that the transfer efficiency of paints using this equipment is only about 50%

Several options were examined and the following were considered most attractive for the near future, both from an environmental impact and cost viewpoint.

● *Low pressure spray guns to replace the airless guns.* The high volume/low pressure spray gun significantly reduces overspray from an estimated 50% with an airless gun to only 15% with the HVLP gun. This immediately translates into a reduction in the amount of paint used and, consequently into a comparable reduction in the amount of VOCs emitted to the atmosphere. In addition, by reducing the overspray, the sludge buildup in the water curtain will be decreased or the time between required cleanouts can be reduced. The cost of the new gun system, with its compressor, is less than \$1000 and retraining of operators is minimal, making this a most attractive option. Closed system spray gun cleaners are now available at relatively low cost (\$500). These systems avoid discharge of solvent to the air while using a minimum amount of solvent. Estimated payout for the conversion is only 0.5 months.

● *Replacement of steel shot with plastic media.* The use of plastic shot as an alternate blasting media is an emerging technology and is readily implementable at Governors Island. The changeover from steel shot to plastic shot can be made with essentially no capital investment. Only minor adjustments are needed. The changeover would markedly reduce the weight of the dust due to lighter density material and increase the recycle capability from 5 for steel to 20 for plastic. Lead from the older lead-based paints will remain a problem until all the buoys have been painted with the new no-lead paint, however the plastic dust can be incinerated where the steel could not. Factors of effective rust removal by the plastic media and coating durability on the plastic-media cleaned buoy need to be considered. This option is highly cost-effective, with payout occurring in only 3.4 months.

● *On-site still for recovery of reusable solvent from spent thinners and waste paints.* Waste paint and solvent thinner generation on the site was recognized as a major source of waste and a significant contributor to the disposal cost. The key in this area is to effectuate improved implementation of management systems for the purchase, inventory and distribution of paint and thinner on the island. Small scale stills were evaluated as a possible alternative to disposal. Estimates were that from 50% to 90% of the volatile solvents can be recovered from paints and contaminated solvents. This option, however, is not highly recommended at this time, in light of the cost and anticipated changes in paint and solvent management.

## RESEARCH, DEVELOPMENT AND DEMONSTRATION

No obvious research, development and demonstration projects were recognized during this opportunity assessment and feasibility analysis of recommended options. This project focused on management initiatives and applied technology changes.

### VETERANS MEDICAL CENTER CINCINNATI, OHIO

As part of the WREAFS program, pollution prevention opportunities were assessed at the Department of Veterans Affairs' Cincinnati - Fort Thomas Medical Center (VA-Cin.). This report serves as a case study for identifying pollution prevention opportunities in a hospital setting and focuses on ways of reducing the discarded medical supply wastestream.

## FACILITY DESCRIPTION

The Veteran Affairs' Medical Center in Cincinnati (VA-Cin) is a government-owned, general medical and surgical hospital offering four principal areas of service: medical, surgical, psychiatric and neurological. The facility maintains 415 authorized and 342 operating beds and is large in comparison to other private and federal hospitals. The facility provides outpatient services for approximately 500 individuals per day. In addition to the medical waste generated on-site, the facility also manages wastes for an associated research facility, nursing home and home health care services.

## AREAS OF WM OPPORTUNITY EVALUATIONS

VA-Cin segregates its waste to minimize the amount transported by the infectious waste contractor because unit costs for infectious waste far exceed unit costs for disposal of general refuse. Opportunities were evaluated through a "mass balance" approach, assuming that material entering a system will be equal to material leaving a system, plus material accumulated. Material balances allow for realizing losses that may have gone undetected if waste streams were characterized solely upon disposal information. VA-Cin estimated that approximately 80% of hospital supplies are disposable and preference for disposables includes cost, convenience, improved quality assurance/quality control of manufacturing, constraints on space and staff for reprocessing and health and safety assurance for sterile integrity. The popularity of disposables emerged about fifteen years ago and the spread of acquired immune deficiency syndrome (AIDS) has escalated this practice recently.

Infectious waste control is defined by the medical waste handling practices based on the Center of Disease Control's (CDC) Universal Precautions of body substance isolation. The wastes are categorized into five groups: general, chemotherapy, blood and body fluids, sharps and radioactive. Disposal methods include infectious waste contract, toxic waste contract, sewer system, animal crematorium and autoclaving on-site prior to offsite disposal.

The study revealed that the three largest consumers of disposable supplies in the hospital are the Supply, Purchasing and Distribution department, the laboratory and the operating room. Eighty-five to ninety percent of all disposables are attributed to these three areas. These areas were studied individually and all disposable usage tracked. The two general types of disposable medical supplies used are plastics and paper (non-woven) products.

### Supply, Purchasing and Distribution

The Supply and Processing Department is a central group that distributes supplies to designated patient wards and services, including the outpatient clinic, recovery room and nursing services. Supplies ordered from here are termed "posted" and eighty percent of hospital's supplies are posted or ordered through central supply.

### Laboratory Services

The Laboratory Services Department performs analyses on specimens taken from patients throughout the Medical Center. It consists of four separate areas: hematology, clinical chemistry, microbiology and histopathology. All laboratory wastes are currently placed in orange biohazard bags, autoclaved and disposed in the general trash as non-infectious waste. There are three sizes of bags: 1 gallon (small), 5 gallon (medium) and 30 gallon (large).

*Hematology Laboratory:* This group draws and analyzes blood samples from 50-60 patients per day. Cloth gowns are currently worn by staff when blood is drawn and replaced with a second cloth gown for work in the laboratory. All gowns are laundered for reuse. This area generates approximately 2 large bags of autoclaved wastes per day.

*Clinical Chemistry Laboratory:* Blood sera and urine analyses are conducted in this laboratory. This area generates 1.5 to 2 large bags of autoclaved waste per day.

*Microbiology Laboratory:* This section generates the greatest amount of disposables by weight and disposable products comprise 98% of all autoclaved waste. The principal disposable is glass Petri plates pre-prepared with agar, a culture media. Approximately 3 large bags of autoclaved wastes are generated daily.

*Histopathology Laboratory:* This area is responsible for analyzing tissue specimens and body parts from surgery and the morgue. A limited number of disposable items are used here with no more than one medium, 5 gallon bag of autoclaved waste generated per day.

### Surgery Department

Surgery handles approximately 15 cases per day. The greatest volume of disposable medical supplies used and disposed of in surgery are lap sponges. Other disposables from surgery include procedure products that are found in operating room packs. Safety, quality assurance and product availability are three major concerns providing the impetus for disposable, operating room packs. Surgery also carefully segregates wastes as they are generated, however in order to increase efficiency, the amount of segregation may be reduced in the future. Blood and body fluids are brought to the storage room in the basement and then transported by the infectious waste hauler to the final treatment and disposal site.

### Other Areas of The Hospital

The *Surgical Intensive Care Unit* uses cloth gowns and launders them for reuse. Blood and body fluid wastes are strictly segregated into 1-2 large bags per day. Waste generated in patient rooms is segregated into three categories: (1) sharps, (2) blood and body fluids and (3) general trash.

*Patient Floors* include such care as administering medication and changing dressings. Waste is segregated into same three categories and amounts generated obviously vary with occupation rate of beds.

The *Medical Intensive Care Unit/Cardiac Care Unit* normally operates at 100% occupancy. The two reusable items employed here are cotton gowns and pressure bags.

*Hemodialysis* unit uses nearly all disposable products. Most are discarded in the blood and body fluids receptacle.

The *Outpatient Clinic* provides services to approximately 500 patients per day. Services provided are surgical procedures, medical exams, chemotherapy, dermatology, urology, plastic surgery, orthopedics and ear, nose and throat. Ninety percent of the supplies used in the outpatient clinic are disposable. Plastic-coated paper gowns are used by staff members administering chemotherapy treatment. Reusable wovens that are commonly used include sheets, pillow cases, towels and blankets.

The *Incinerator* is located on the ninth floor of the building. Sharps, pathological wastes and expired pharmacy drugs are incinerated every Friday. The capacity is not great enough to accommodate any additional waste, and consequently, the hospital is planning to build one with

increased capacity to accommodate all the medical waste, this eliminating the need to contract with waste haulers.

The *Storage Area* for blood and body fluid waste and cytotoxic wastes is located in the basement. These wastes are packaged in large brown plastic garbage bags, transported to the basement, placed in cardboard boxes lined with red biohazard bags. These are transported offsite to be incinerated at a commercial treatment/disposal facility. The hospital is charged \$0.03 per pound of blood and body fluid waste transported for disposal.

## WASTE MINIMIZATION OPTIONS AND RECOMMENDATIONS

Through a review of available literature, the site visit at VA-Cin and an understanding of the limitations facing waste reduction in a hospital setting, recommendations are made pertaining to product substitution, the reuse of disposables and recycling:

● Reuse of Disposables: As the cost of solid waste disposal (including incineration) escalates, particularly the cost for medical wastes, the reintroduction of reusables may be warranted. Hospital automation, specifically in the processing and sterilization of soiled linens, over the past few years is enabling many institutions to reconsider the use of reusable surgical linens as a cost-effective option to the disposal of paper products. The factors which must be considered when making the decision to reuse a single-use product include possible contamination, increased liability, decreased functional reliability, compromised patient safety and the associated costs. It must be determined if the quality assurance program is compatible with reprocessing disposable items, and if not, evaluate the economic feasibility to make it so. As an item becomes more critical and the potential for infection increases, the likelihood that an item will be reused decreases. In the end, safety takes precedence over economics of pollution prevention in a health care environment.

● Wovens versus Nonwovens: The use of wovens would decrease the volume and weight of hospital waste significantly. Therefore, employing wovens throughout the hospital should be given serious consideration and each of the reasons for choosing disposables re-evaluated. Health care personnel often choose paper products to ensure the sterility of an item even though wovens, when laundered at sufficiently high temperatures and sterilized, present an equally sanitary product. Reusable fabric can be treated and made water repellent, therefore resistant to blood and body fluid penetration, and density of the treated fabric provides an effective barrier to bacteria. The advantages of woven material include nonabrasiveness and allowance for freedom of movement. It is more puncture resistant than paper and allows for ease of maneuverability and examination. When costs are integrated, the use of wovens may also represent a better use of hospital resources. Although, in some cases, paper products will offer a superior basis for use in administering the best and safest medical care, the universal use of paper products in any health care facility should be avoided.

● Product Substitution: Plastic covers for pillows can be replaced by using vinyl/nylon laminate covers. These covers would prolong the life of the pillows, decrease the risk of infection and reduce waste by continuing the use of woven pillow covers. In some cases within the laboratories, reprocessing of glassware may prove an economical alternative to plastic disposables.

## RESEARCH, DEVELOPMENT AND DEMONSTRATION

Although pollution prevention opportunities may appear limited at first, the implementation of alternatives whenever possible will, in sum, achieve significant waste reduction. In addition, greater opportunities may be unveiled with further research. Suggestions for research and development possibilities in the health care industry are presented below:

- Costing: There may be a need to conduct cost studies for certain health care products in cooperation with other Federal agencies, such as Veterans Affairs and Health and Human Services.

- Quality Assurance: There may be a need to consider working with trade associations and other Federal agencies, such as the Food and Drug Administration in reviewing technical, legal and policy impacts of reusing disposables. The ultimate goal would be a protocol for reuse.

- Development of Reprocessing Capacity: There may be potential for reestablishing the viability of reprocessing, perhaps by stimulating the development of cooperative reprocessing service centers in areas with a high density of health care facilities.

- Developing Reusable Market: The EPA and VA may want to work together in developing procurement guidelines for the VA which will stimulate the production and distribution of reusables and recyclables. This could lead to waste minimization technology transfer opportunities throughout the health care community.

Officials expressed the belief that it was unlikely that hospitals would convert back to the use of reusables on a wholesale basis due to concerns over worker health and safety and cost efficiency.

## ON-GOING ASSESSMENTS

### OPTICAL FABRICATION LABORATORY FITZSIMMONS ARMY MEDICAL CENTER DENVER, COLORADO

This project was established to develop waste minimization options for the principal hazardous waste generating areas at the Fitzsimmons Army Medical Center, Denver, Colorado, Optical Fabrication Laboratory (FAMC/OFL) installation. It was conducted in cooperation with the Environmental Office of the Directorate of Engineering and Housing, which has a on-going waste management program.

## FACILITY DESCRIPTION

The Optical Fabrication Laboratory of the Fitzsimmons Army Medical Center, Aurora, Colorado, is housed in the Charles W. Carter Optical Center. The OFL produces about 1,400 pairs of spectacles per month, with 85 to 90% of the production involving fabrication of glass lenses. The remaining 10 to 15% involves plastic lens fabrication.

## AREAS OF WM OPPORTUNITY EVALUATIONS

The areas involved in this project were the glass and plastic lens fabrication where uncut lenses are received from optical suppliers and matched with eyeglass prescription orders. The lenses are precoated with a polymer film of volatile solvents - methyl ethyl ketone (MEK), methanol and ethanol. The precoated lenses are then blocked, ground to desired curvature, washed and deblocked. The cleaned lenses are ground to fit frames, chemically hardened and placed in frames.

There are several waste streams produced by the lens production and of these the following were selected for waste minimization or cost-savings options:

- Fine glass particulates from lens grinding are produced in amounts averaging 300 pounds per day.
- Spent alkaline wastewater from glass lens deblocking and cleaning operations may contain suspended alloy particles as well as possibly small amounts of dissolved lead salts.

## WASTE MINIMIZATION OPTIONS AND RECOMMENDATIONS

Of the two waste streams studied, the nonhazardous glass fines were examined from a recycle standpoint, eliminating a disposal cost. Several options were considered for the RCRA suspect hazardous materials in the alkaline wastewaters.

- Fine glass particulates are possible feedstock for glass or ceramic tile manufacturing. Transportation costs would limit marketable area as approximately 37.5 tons are produced per year.
- Three potential options were recommended for the alkaline wastewaters: (1) substitution of blocking alloy; (2) filtration of wastewater prior to disposal; and (3) removal of dissolved lead. Of the three, substitution proved to be uneconomical. Installation of a filter on the spent washwater effluent stream may be economical if sufficient alloy particulates can be recovered to justify its operation. Onsite formulation of the alkaline washing solution was explored, however exact ingredients and quantities are unknown at present.

## RESEARCH, DEVELOPMENT AND DEMONSTRATION

Three specific needs were identified as a result of this study:

- Develop a milder glass cleaning solution to replace alkaline one.
- Assess the feasibility of developing another less costly alloy containing no toxic metals.
- Development and/or adaption of an aqueous cleaner for tool cleaning operations to replace Stoddard solvent.

The experience and insight gained during this assessment should be of definite value for a similar assessment proposed to be conducted at the U.S. Navy's plastic lens fabrication facility in Yorktown, Virginia.

## SCOTT AIR FORCE BASE, ILLINOIS

This project will produce an assessment of three operations at Scott Air Force Base, Illinois. These are circuit board manufacturing, the non-destructive wheel inspection and a painting operation. The primary focus of the project is the non-destructive wheel inspection which possibly involves a toxic penetrant used for detection of landing wheel fatigue, such as cracks or other discontinuities that penetrate the surface of the metal.

### EVALUATION OF EMULSION CLEANERS AT AIR FORCE PLANT NUMBER 6

This project will evaluate the conformance of emulsion cleaners as replacement for trichloroethylene (TCE) as degreasers in aluminum and steel preparation for manufacturing. This process is used in production of military transport aircraft. The results can be transferred to similar operations in DOD and/or DOE and other facilities.

### WASTE REDUCTION FROM CHLORINATED & PETROLEUM-BASED DEGREASING OPERATIONS

This project will serve in formulating a model technology service program for DOD's chlorinated solvents program. Auburn University will ascertain what is required to make state-of-the-art solvent recycling technology available and minimize the risk to operators, liability and damage to parts being cleaned.

### OTHER RESEARCH AND DEVELOPMENT WITHIN THE FEDERAL COMMUNITY

Other Pollution Prevention Research Branch research projects with the Federal Community are:

- Wet to Dry System Evaluation in a Navy Paint Spray Booth

This project will evaluate the conversion of a Navy paint spray booth from a water curtain particulate emission control technology to a dry filtration technology.

- Reclaiming Fiber from Newsprint

This project, funded under an interagency agreement with the United States Department of Agriculture's Forest Products Laboratory in Madison, Wisconsin, is designed to investigate the potential for newsprint reclamation through a dry fiberizing process.

- Composites from Recycled Plastics, Wood and Recycled Wood Fiber

This is a three-year interagency agreement between the Forest Products Laboratory of the U.S. Department of Agriculture and EPA to investigate and develop wood/plastic composites.

## NEWLY PROPOSED PROJECTS

### ● Waste Minimization Assessments and Reviews Within The Federal Community

A waste minimization assessment is being conducted at the Department of the Treasury's Bureau of Printing and Engraving in Washington, D.C., where the principal waste generating activities result in metal and ink wastes.

Waste Minimization Assessments are planned with:

- ✓ The U.S. Navy and the City of San Diego to consider joint pollution prevention options.
- ✓ The Department of Interior's Bureau of Mines.
- ✓ The Department of Agriculture's Agriculture Research Service in Beltsville, Maryland.
- ✓ The U.S. Army's facility in Ft. Carson, Colorado.
- ✓ The Military Facility Model Community Pollution Prevention Demonstration Program within the Chesapeake Bay.

### ● USCGS Ketchikan Pollution Prevention Project

This project will provide support to the Alaska Department of Environmental Conservation and the United States Coast Guard Service to assess pollution prevention opportunities at the USCGS facilities at Ketchikan, Alaska.

## MATRIX OF INTERCHANGE

Table 1 describes the Pollution Prevention Research Branch's matrix of interchange with the Federal Community. This represents completed, on-going and scheduled projects.

**POLLUTION PREVENTION RESEARCH MATRIX OF INTERCHANGE  
IN THE FEDERAL COMMUNITY**

(COMPLETED, ONGOING AND SCHEDULED PROJECTS)

DEPARTMENTS	ASSESSMENT	RD&D	TECH TRANS
AGRICULTURE	X	X	X
COMMERCE			
DEFENSE: AIR FORCE	X	X	X
ARMY	X		X
NAVY	X	X	X
EDUCATION			
ENERGY	X	X	X
HEALTH & HUMAN SERVICES			
HOUSING & URBAN RENEWAL			
INTERIOR	X		X
JUSTICE			
LABOR			
STATE			
TRANSPORTATION	X		X
TREASURY	X		X
VETERANS AFFAIRS	X		X

**SUMMARY/PROJECTIONS**

Assessments have been initiated and have ongoing or completed research with seven of fourteen of the Departments. We anticipate further cooperative projects with these federal facilities and encourage the other seven Departments to seek cooperative participation in research projects for pollution prevention in industrial processes. Each of these assessments can be used as reference technologies in similar areas and each source reduction of a toxic waste will be a positive step toward environmental protection.

# TOXIC SUBSTANCE REDUCTION FOR NARROW-WEB FLEXOGRAPHIC PRINTERS

by

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## ABSTRACT

This project is one of five undertaken as part of the Illinois WRITE (Waste Reduction Innovative Technology Evaluation) Program, and has quantitatively evaluated, for one narrow-web flexographic printing firm, the amount of waste reduction (both volume and toxicity) and the economic impact resulting from modification of a traditional technology. Two main changes in the printing process were: substitution of water based inks for solvent based inks and substitution of a nontoxic liquid cleaner (terpene based) for a halogenated solvent cleaner. The paper presents an in-plant evaluation and the impact of these changes on environmental, health, cost, and other factors.

## INTRODUCTION

This project is one of five undertaken as part of the Illinois WRITE Program (Waste Reduction Innovative Technology Evaluation), and has quantitatively evaluated, for one narrow-web flexographic printing firm, the amount of waste reduction (both volume and toxicity), and the economic impact resulting from modification of a traditional technology. Two main changes in the printing process of this company were considered for evaluation in this project:

1. Substitution of water-based inks for solvent-based inks.
2. Substitution of a non-toxic liquid cleaner (terpene based) for a halogenated solvent cleaner.

The report is based on work performed under terms of the Illinois/EPA WRITE Program. Specifically, the project has been a joint effort of MPI Label Systems, University Park, Illinois, the Hazardous Waste Research and Information Center, Illinois Dept. of Energy and Natural Resources, Champaign, Illinois, and the U.S. EPA Office of Research and Development, Cincinnati, Ohio

All project testing was conducted in the printing plant of MPI Label Systems, Inc., University Park (Monee), Illinois. The facilities are housed in a modern one-story, clear-span building of about 15,000 square feet, half of which is used for storage of supplies, and half for the actual printing operation and the administrative offices.

MPI has been in operation at the current site slightly more than two years, having moved from an older nearby location. The firm is one of eight separate corporate printing plants and has always relied on narrow-web flexography to produce a wide variety of labels. Flexographic printing derives its name from the flexible, roll-mounted printing plates used, as opposed to the classical non-flexible metal printing plates. Several of the press lines have the capacity to print up to eight colors per label. Each line is operated by

a single individual who is responsible for all steps of a complete label run.

During 1988 the parent organization mandated that all its plants eliminate, as quickly as practical, every toxic material then in use. Further, all future operations were to avoid use of toxic and hazardous materials, even barring storage of small quantities of such materials in each plant. Part of the motivation for this mandate was concern about the exposure by their employees to alcohol fumes in the work area.

The first modification, and the most significant, was to change to water-based inks as a substitute for the then common alcohol-based inks. A related change, though instituted primarily for technological improvement and not waste-related, was the substitution of newly developed plastic printing plates for the older type rubber printing plates. Water-based inks did not produce satisfactory images with rubber printing plates. Thus, the development of plastic printing plates was necessary before water-based inks could be adopted. The plate making operation is not a part of this evaluation because at MPI the plates are not made in house.

The second step involved elimination of the several halogenated solvents used to clean presses at the end of a run. Before these changes, the solvent- and ink-soaked wipers resulting from cleaning had to be disposed of as hazardous waste materials, an expensive handling and disposal operation. To make this particular change, a variety of relatively new cleaning agents were examined. These agents ranged from industrial detergent cleaners to terpene-based mixtures. This step continues to be one of periodic reevaluation as more satisfactory cleaners become available. Although MPI now does all its cleaning with a dilute aqueous solution of detergent, it is prepared to look at any promising product.

#### **PRINTING PROCESS BACKGROUND**

The Printing Industries of America (1991)<sup>1</sup> estimates there are about 57,000 printing, publishing and related facilities within the United States. Of these about 40,000 are commercial printers. The remainder include newspaper and magazine publishers, photocopiers and in-house printers. The five most common printing processes in order of their market share are lithography (also called offset), gravure, flexography,

letterpress and screen. Presses are also categorized according to whether they print on individual sheets, called sheet-fed, or print on a continuous roll, called web, of paper or other substrates.

The printing process begins by making an image, including words and designs, of what is to be printed. For each color that is used, a different image is made. These images are made by various processes on various types of metal, rubber or plastic plates. Common image-making processes are similar to developing a photographic image. Recently developed plastic plates are made of photosensitive polymers. The image to be printed is exposed onto the plate, and the exposed polymers harden. The unexposed and softer areas of the plate are washed away with various solvents, leaving a raised image for printing. Recently water-based plate developing systems have been developed for some segments of the industry.

The next step in the printing process is to apply ink to paper or some other substrate. The common printing processes listed above accomplish this step in different ways, however, they generally function in much the same manner.

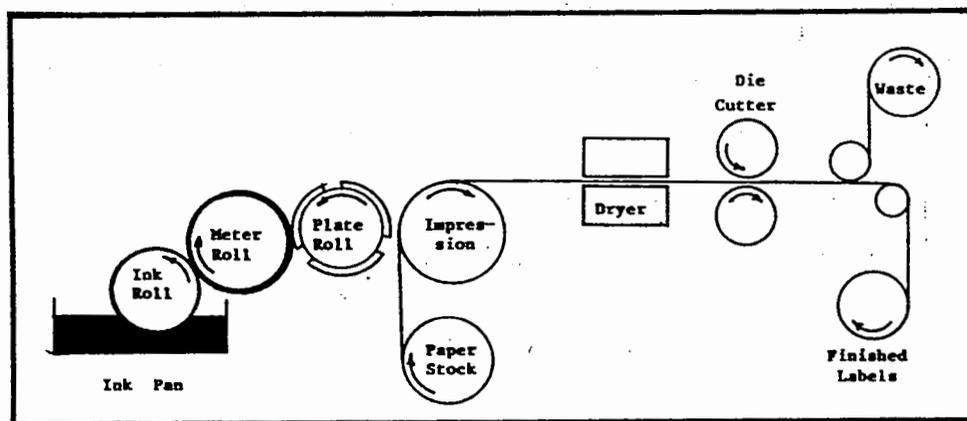


Figure 1. Single print-station schematic.

Figure 1 presents a simplified schematic of a single print station. The schematic shown in Figure

1 is drawn to represent a typical flexographic arrangement. However, it generally represents most other printing processes. Ink from a reservoir is picked up by a roller in contact with the ink. That roller then contacts another roller (sometimes several dozen rollers are involved) to develop an ink film of ideal thickness for transfer to the printing plate. The base material on which the printing is to be imposed (usually paper, fabric or plastic) is pressed against the printing plate by another roller to receive the plate's ink impression. Rollers are used so the entire process can be continuous (using either sheets or rolls of paper), not intermittent as had been the case from Gutenberg's time (15th century) till the early 20th century when rotary presses were developed.

The printing station shown in Figure 1 is limited to a single color ink. Multicolor printing uses several printing stations in series, each applying a different ink color with controls to assure perfect registration, all assembled to form a single print line. In Figure 2 a four-color flexographic press is shown. After each inking station, the labels pass through a drying station which dries the ink in a few seconds. Each station contains heaters maintaining a temperature of approximately 70°C. Depending on the type of material receiving the plate's impression, and the customer's desire, the dry printed surface may be sprayed with a coat of gloss varnish or plastic to protect it. At the end the completed labels are wound onto a roll. The speed or rate at which paper is fed through the press can be varied, depending on the type and amount of ink used.

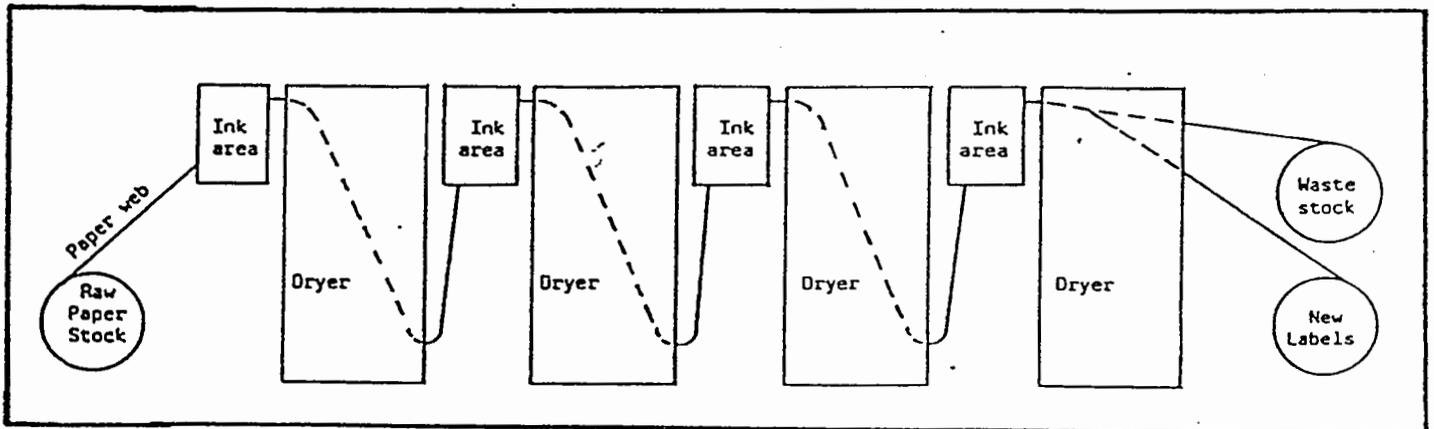


FIGURE 2. Typical 4-color flexographic printing press.

Within the flexographic printing industry, press types are separated into narrow-web (paper up to 16" wide) and wide-web(over 16" wide). Narrow-web is typically used to print labels, packaging, envelopes, and plastic bags. Wide-web presses are used for newspapers, wallpaper, soft-drink cartons and similar surfaces. Most of the MPI presses (narrow web) use a web that is 9" wide.

Paper label stock for printing is made of two-ply material. The bottom ply consists of silicone-treated paper. The top ply is the paper on which the labels are printed, and it clings to the bottom ply by virtue of an adhesive able to be peeled away from the silicone treated base stock. After printing and drying, possibly receiving a gloss coat, each label is "parted" (cut) or readied for removal from the parent paper web along each label's entire perimeter by a steel-die roller cutter. The steel-die, working to very close tolerances, cuts through the single top layer of paper to separate the finished label from the surrounding unprinted stock. Although the latter (stock waste) is peeled away automatically onto a separate roll for disposal by shipment to a landfill, the entire label industry is presently seeking a recycler who can handle this material with the adhesive on one side. The bottom ply, with adhering labels, is made up into rolls of a specific label count for each customer, then packed and shipped. The eventual customer will remove the finished labels for application either automatically or manually.

The most recent industry survey (Flexographic Technical Association(FTA), 1989)<sup>2</sup> concluded that over 4,000 U.S. printing plants utilize more than 22,000 narrow-web flexographic presses, employ about 150,000 individuals, and generate about \$4.5 billion annually of product. Annual growth over the past decade is estimated to be 3 - 5%.

Flexo inks were originally formulated to resemble the inks used in other printing processes. Hence, they were usually compounded of colored metal compounds for pigments, a quick-drying oil vehicle in which the coloring substance was dispersed, plus an organic solvent to control the ink's viscosity and speed of drying. The organic solvent was frequently of the trichloroethane family because of its rapid evaporation rate. As the hazards of these solvents were finally recognized and accepted, substitute solvents were sought as safe replacements. Aliphatic alcohols, and their derivatives, are now used as solvents in

many current solvent-based inks. At the end of 1989 it was estimated that 90-95%<sup>3</sup> of all flexographic label printers had changed to water-based inks. Demand for the latter amounts to more than 300,000,000 pounds of flexo ink per year, excluding the newspaper industry.

MPI's water-based inks contain organic chemical pigments, no heavy metals, an emulsifier, an acrylic resin thickener similar to that found in water-based house paints, up to 5% of isopropyl alcohol and 50 - 65% water. Flexographic inks have a viscosity which approximates that of ordinary white oil or glycerine. By contrast, the inks used on offset presses possess a viscosity closely resembling warm taffy. Although the waste reduction aspect of this new ink technology has not been completely and quantitatively documented, the flexo industry's success with water-based inks has spurred other printing firms, notably some using the rotogravure process, to change to water-based inks.

Because the cleaning agents used most frequently by printers were often composed of hazardous organic solvents, the solvent-wetted wiping materials used as sponging pads also had to be classified as hazardous waste and disposed of in hazardous waste landfills at relatively high cost. At MPI the fiber wipers, in addition to the hazardous solvent cleaners, have now been abandoned in favor of fabric shop towels which, when wetted with the current detergent cleaning solution, can be laundered and reused - an additional economy.

#### **WASTE REDUCTION IN PRINTING**

Wastes are produced at each step in the printing process. Solid and liquid wastes generated in making an image on a plate include damaged plates, developed film, photographic chemicals, silver (if not recovered), and the solutions used to develop the plates. Spent photoprocessing chemicals are generally regarded as being biodegradable and are usually discharged to the sewer. Certain solutions may contain mercury compounds which require special handling. Plate-making wastes can include acids and alkalis which also may require special handling. Depending on the specific materials used, some solvents may also be released to the air during image making and plate processing.

During the printing process, solvents in the inks (e.g., alcohols, aliphatics, ketones or xylenes)

and cleaning solutions are released to the air. Most of the ink solvents are evaporated while drying the inks. The amount of solvents released depends on the ink formulation and the type of printing process being used. Solvent emissions from commercial gravure applications are of particular concern. Most inks used in lithography dry by oxidative polymerization which produces little solvent emissions. There are also non-heatset web inks which dry by absorption in the newsprint substrate. In lithography, fountain solutions are used which contain 5-15% isopropyl alcohol (IPA), defoamers, fungicides, gum arabic, phosphoric acid and water. The alcohol evaporates along with the water. Fountain solutions have recently been developed that use soaps and detergents instead of IPA. Point source control technologies (catalytic or thermal incineration, carbon adsorption, or cooler/condenser systems) have been installed in some plants to capture these solvent releases.<sup>4-7</sup>

A wide variety of cleaning solutions are used by printers. These cleaners can contain volatile organic chemicals such as benzene, toluene, kerosene, naphtha, methanol, trichloroethane and methylene chloride.

Waste inks are the primary liquid wastes generated in the printing process. Most inks can be recycled such as by blending to make a black ink, either by the ink manufacturer or in-house. Waste inks that contain organic solvents may be classified as hazardous wastes and must be properly incinerated or landfilled. Some nonhazardous inks are sent to the sanitary sewer. Small amounts of lubricating oils are the other liquid waste that is generated from operation of the printing presses. The used oil can often be recycled.<sup>5</sup>

Waste paper is the main solid waste generated in printing. In lithography, almost 98% of the total waste generated is reported to be waste paper and paper scrap. This comes from rejected or off-quality runs, scraps from the start and end of runs, and overruns. The paper consumed as waste during setup is mostly a function of the press operator's experience, complexity of the label to be printed, the number of ink colors required, and the size of the label. Operators try to use paper stock of such a width as to minimize trim waste. Other solid waste produced includes empty ink containers and cleanup rags or wipes.

Some printers dispose of their rags in the trash while others have the rags dry-cleaned for reuse. The sludge produced in the dry cleaning process contains the materials removed from the rags (inks, cleaners, oil, dirt and other contaminants) and this sludge may require disposal as a hazardous waste.<sup>5</sup>

Options for reducing waste generated by printers have recently been reviewed by the State of California<sup>8</sup> and the USEPA<sup>5</sup>. Methods for waste reduction in materials handling and storage, image processing, plate making, printing, and finishing have been listed. Techniques which can be used to reduce waste during printing include using less hazardous inks and cleaners plus generally being more careful during setup and cleaning. Waste ink was reduced in one case by spraying a protective coat over the ink in the fountain at the end of each day. As a result, waste ink was reduced by 5 pounds per day. Thus, less waste ink would need to be disposed of and less new ink purchased. The total operating savings were estimated at \$3,375 per year for this technique<sup>8</sup>. Techniques for reducing waste paper include installing break detectors and automatic splicers in web operations.

Changing to less hazardous inks is not always straightforward. Water-based inks generally require more energy to dry than do inks with a high solvent content, though this is offset (can run 10% faster than alcohol inks) by their quicker absorption on a paper base. Other reported disadvantages of water-based inks are a need for more frequent equipment cleaning, and a tendency to cause the paper to curl; many are also low-gloss. Another alternative which can reduce solvent emissions is the use of UV inks. These inks set or harden when exposed to UV light. Disadvantages of these inks include higher cost, formation of ozone, hazards of UV to personnel, difficulty in recycling the printed paper, and high toxicity of some of the chemicals in the inks. Electron-beam-dried inks are also available that contain no solvents, but operator protection from X-rays created by the process is required, and the system often degrades the paper<sup>5</sup>.

Three waste reduction case studies of printing plants were recently conducted for the state of California<sup>5,8</sup>. At one facility the option of installing in-house recycling equipment was evaluated. It was found for this plant that in-house recycle would pay back in 8 months. These case studies reviewed

operations at two other plants and described practices already in place to reduce the amount of waste being generated. In-plant measurements of the waste being generated were not taken in these studies. Instead, the amount of materials used (ink, paper, fountain solution, etc.) was reported<sup>5,8</sup>.

A case study of switching from alcohol-based inks to water-based inks on low density polyethylene film by a flexographic printer was presented by Makrauer<sup>9</sup>. He reported considerable difficulty in making the conversion. Technical difficulties included pH control for the ink, a need to modify the drying equipment, ink metering modifications and increased roller wear. All problems were gradually overcome through improved ink formulations, experimentation, and facing the rollers with more durable materials. Makrauer also reported that cleaning water-based inks was more difficult. Benefits of water-based inks at that time were compliance with environmental regulations, improved color control, greater coverage yield, and improved working conditions due to reduced alcohol vapors. Quantitative measurements of emissions and other wastes generated when using alcohol-based inks compared with water-based inks were not reported. In fact, a quantitative evaluation of the benefits of using water-based inks in flexographic printing has not been published.

It is worth noting, however, that though printing on plastic materials via flexography had some problems early in the introduction of water-based inks, using the same technology for newspapers has been considerably simpler. Many of the major newspapers have already transferred to this type of printing with excellent results. In several recent installations the printing line has been designed so there are no ink wastes. Excess ink and ink washings are collected in a holding tank and used to dilute new ink to the proper viscosity. This closed-cycle system, of course, does not reduce any of the paper wastes. Although none of these newspapers have published an economic comparison of the old versus the new system, private discussions with plant managers confirm each plant is producing a better product at less cost.

#### **PROJECT OBJECTIVES**

This project had two main objectives: compare the volume and toxicity of any wastes released to the air, liquid wastes and solid wastes generated during printing before and after switching to

water-based inks and a detergent cleaner; determine the cost impact on the company as a result of the process changes.

Solvent loss by emission from the inks was estimated by materials balance, laboratory measurement of alcohol evaporation from the two types of inks, and calculations based on the composition of the inks. The methods used to compare emissions from the two ink types are summarized in Table 1. Since MPI no longer uses alcohol-based inks, and will not permit their use in the plant, it was not possible to measure alcohol emissions by in-plant use of those inks. However, the volume of alcohols evaporated from the two types of inks during a printing run can be calculated from known ink formulations if the total amount of ink used is known. In-plant measurements of ink and cleaner usage were taken for two single-color printing runs to obtain an estimate of variability.

Table 1. Methods Used for Estimation of Ink Emissions

TYPE OF INK	MATERIALS BALANCE (In-plant)	EVAPORATION RATE LOSS	INK COMPOSITION (Calculation)
Water-based	X	X	X
Alcohol-based	-	X	X

For the materials balance method, the weight of ink used during each printing run, U, was calculated by weighing the various items before and after the printing runs using the following formula:

$$U = (A + W) - (R + I + S) \quad (1)$$

where, A = weight of ink in reservoir and weight of reservoir at beginning

W = weight of water and other materials added during run

R = weight of ink returned to reservoir and weight of reservoir at end of run

I = weight of ink retained in ink pan, plus gaskets, at end of run

S = weight of ink lost by spilling

Mass measurements were taken on an electronic balance (capacity: 12 kgs.,  $\pm 0.1$  gm) which was transported to the printing site. The weight of alcohol lost upon drying to constant weight

in the laboratory was also determined gravimetrically. The percent solids of both ink types were determined by drying known weights (approximately 100 gms in triplicate) of ink samples in an oven at 70° C, the drying temperature maintained on each flexo press.

Laboratory measurements of evaporative loss of solvents for each ink were used to estimate the percent volatiles. The weight of evaporative loss, E, was calculated using the total weight of ink used (U from equation (1) ) as follows:

$$(U \times \% \text{ volatilized})/100 = E \quad (2)$$

The weight of ink that was retained on the labels (Q) was calculated by:

$$Q = U - E \quad (3)$$

The amount of ink on waste labels was then estimated by the proportion of total labels printed to good labels sold as product, or not wasted.

These results were compared with the weight of volatiles in each ink as reported on the material safety data sheets. This information is shown in Table 2. Both inks have similar amounts of total volatiles. The alcohol-based ink contains six volatile components, four of them being alcohols. Ethyl alcohol and isopropyl alcohol are present in the largest amounts. By comparison, the water-based ink contains four volatile components. Most of the volatiles are water and isopropyl alcohol. Some of the water (about 24%) is bound to the resins and does not evaporate upon drying. Both the solvent cleaner previously used and the detergent cleaner contain over 97% volatiles.

The amount of ink and other materials that were disposed of as liquid waste was determined gravimetrically for the two printing runs. No liquid ink wastes were sent to the sanitary sewer prior to using water-based inks. The solvent-based waste ink had to be disposed of as a hazardous waste and was thus manifested. While the total amount of waste manifested in a year was available from company records, it was not possible to determine the amount of liquid solvent-based ink that would have been generated from printing runs similar to those we evaluated with the water-based inks. Company officials reported that in their experience the amount of solid and liquid wastes generated are essentially the same for the two types

Table 2. Composition of Inks and Cleaners Evaluated<sup>10-13</sup>

COMPOSITION		
Material	Component	Percent by wt.
<b>INKS</b>		
Alcohol-based Ink (Manufacturers data)	Methyl alcohol (v)	4.7
	Isopropyl alcohol (v)	10.6
	n-propyl alcohol (v)	6.5
	Ethyl alcohol (v)	21.4
	Ethyl acetate (v)	4.2
	VM&P naphtha (v)	6.6
	Resins (nonv)	Unknown
	Pigment (nonv)	Unknown
	Volatiles	54.5
Water-based Ink (Manufacturers data)	Isopropyl alcohol (v)	5.0
	Ammonia (v)	1.0
	Dimethylethanolamine (v)	1.0
	Acrylic resin (nonv)	20.0
	Azo pigment (nonv)	8.0
	Water (v)	65.0
	Volatiles	56.5
<b>CLEANERS</b>		
Solvent cleaner (Manufacturers data)	Toluene (v)	54.5
	Acetone (v)	20.0
	Isopropyl alcohol (v)	20.0
	Diacetone alcohol (v)	5.5
	Volatiles	99. +
Detergent cleaner	Volatiles	97.8

(v) = volatile; (nonv) = nonvolatile. **NOTE:** both ink types contain plastic-based resins which react and bind with some of the other materials present on drying. Hence, one cannot simply add the volatile percentages to obtain total volatiles.

of inks. The main difference is that liquid wastes from the water-based ink do not have to be disposed of as a hazardous waste.

Currently, each printing line has a 50 gallon drum of water used to rinse off ink wastes. Each drum is emptied every week into a commercial ink removal/filtering device called an Ink Splitter. This unit absorbs the colored pigments on cellulose fibers, and the slightly grayish filtrate is run to the sewer - as approved by the local treatment plant. The colored absorbent is acceptable in landfills as non-hazardous material, primarily because none of the ink pigments contain metals of any type.

Ink wastes on the press rollers, pans and plate are removed by scrubbing with a brush and fabric towel wetted with an aqueous detergent solution. This quickly removes the ink residues. The rollers, pans and plates are then dried with another fabric towel. The towels are rinsed in the barrel of water at each press, then sent to an industrial laundry service for cleaning. By appearance, a negligible amount of ink was retained by these towels. The amount of detergent cleaner used was measured for each run (although this depends largely on the press operator's general practice), but it was not possible to measure amount of solvent cleaner previously used. Hence, the toxicity of the two cleaners was compared using the degree of hazard system.

#### DEGREE OF HAZARD REDUCTION

Toxicity reduction evaluations on the ink and cleaner wastes were accomplished with the Degree of Hazard<sup>14</sup> scheme by calculating the equivalent toxic concentration ( $C_{eq}$ ) as follows:

$$C_{eq} = A \text{ SUM } (C_i/B_i T_i) \quad (4)$$

where,

SUM means the sum of the results of the calculation in parentheses for each component of the waste stream.

$C_i$  is the concentration of component  $i$  as a percent of the waste by weight.

$T_i$  is a measure of the toxicity of component  $i$ .

$A$  is a constant equal to 300. It is used to allow entry of percent values for  $C_i$ , and to adjust

the results so that a reference material, 100% copper sulfate, with an oral toxicity of 300 mg/kg, achieves an equivalent toxicity of 100.

$B_i$  is a conversion factor used to convert toxicities ( $T_i$ ) to equivalent oral toxicities.  $B_i$  is determined from Table 3. For carcinogens and mutagens, a  $TD_{50}$  oral rat is used when available. Otherwise, carcinogens are assigned a  $T_i$  of 0.1 mg/kg; and mutagens are assigned a  $T_i$  of 0.6 mg/kg. Toxicities are converted to equivalent oral toxicities as specified in Table 3. The equivalent toxicity given in this Table has the same toxicological response as referenced in the RCRA listing criteria<sup>15</sup>.

Table 3. Conversion Factors

Conversion factors for the equivalent oral toxicities ( $B_i$ )		
TOXICITY MEASURE	UNITS	$B_i$
Oral - $LD_{50}$	mg/kg	1.00
Carcinogen/mutagen - $LD_{50}$	mg/kg	1.00
Aquatic - 48 or 96 hr - $LC_{50}$	ppm	5.00
Inhalation - $LC_{50}$	mg/l	25.00
Dermal - $LD_{50}$	mg/kg	0.25

Toxicity values are ranked by source according to the following priorities, with the best sources listed first: oral rat; inhalation rat; dermal rabbit; or, aquatic toxicity and other mammalian toxicity values. If there is more than one value for the toxicity from the best available source, the lowest (most toxic) equivalent oral toxicity value is used. If a carcinogen or mutagen is assigned a value for  $T_i$  in the absence of a  $TD_{50}$ ,  $B_i$  is assigned a value of 1.

The toxic amount,  $M$ , is calculated as follows:

$$M = SC_{eq} \quad (5)$$

where,  $S$  is the maximum size of a waste stream produced in kg/month.

$C_{eq}$  is the equivalent concentration from equation (4).

The result of these calculations will be an estimate of the toxic amount (M) for each ink and cleaner type generated during a printing run. This toxic amount takes into account the toxicity and amount of each component of the inks and cleaner. The toxic amount, for M, can range from 0 to greater than 10,000. This toxic amount can be considered a relative toxicity of each ink and cleaner type. These relative toxicities can then be compared for the air, liquid and solid wastes produced while printing with the two types of inks and cleaners. At MPI Label Systems, no waste was disposed of in wash water prior to the ink substitution, so any determination of the amount and toxicity of waste disposed of in waste water will be absolute.

The economic analysis of these various technology changes is based on comparison of the factors shown in Table 4. As far as possible, monetary values are based on annual costs. This is the only valid approach since no capital investment was required; hence, such terms as annual rate of return and payback are not applicable. The factors listed in Table 4 were selected after a tour of the plant and discussions with the plant manager.

Table 4. Summary of Cost Comparison Factors Evaluated

<b>COST COMPARISON FACTORS</b>
<b>INKS</b>
Print speed
Raw materials
Waste disposal and handling
<b>CLEANERS</b>
Disposal
Raw materials
<b>OVERALL</b>
Insurance liability
Inventory

## RESULTS OF ON-SITE TESTING

Two individual label runs were evaluated at widely separated times, with different size and different colored labels, different operators and with different label totals.

1. Green labels. Approximately 3.25 X 13 inches, printed with green ink (yellow plus blue) on non-glossy white stock for a total run of approximately 55,000 labels.

2. Purple labels. Approximately 0.75 X 1.75 inches, printed with purple ink on glossy white stock for a total run of approximately 250,000 labels.

In each case the total weight of materials added (equation 1) and the weight of materials remaining at the end of the run was measured. The difference was the weight of material that was assumed to be either evaporated to the shop air, dried on the labels, or wasted.

During the printing of the green labels, an ink pump was used to increase the size of the ink reservoir. Ink was continually recirculated between the ink pump and the ink pan. The weight of the ink pump and ink contained in it was determined at the beginning before any labels were printed ( $A$  in equation 1). During the course of that run water was added to the ink to adjust the color and viscosity on 9 occasions totaling 842.7 grams ( $W$  in equation 1). At the end of the run the rollers, plate, and pans were cleaned and the ink drained back into the ink pump for future use. The ink pump with all materials added during the printing was then weighed ( $R$  in equation 1). One spill ( $S$  in equation 1) occurred during this run. The ink pan and gaskets adjacent to the roller were weighed before and after the run to measure the amount of ink retained on them after they were scraped ( $I$  in equation 1). During the printing of the purple labels nothing was added, and there was no loss due to spillage.

The total weight of ink used during the printing of these two labels is shown in Table 5. For the two water-based inks the total amount used was calculated according to equation 1. To estimate the amount of ink volatilized the % loss as determined by laboratory evaporation of each ink was used according to equation 2. The laboratory evaporation results are shown in Table 6. The amount of solids retained on the labels was calculated by the difference between the total ink used and the weight evaporated.

Table 5. Ink Used and Estimated Emissions

	GREEN LABELS		PURPLE LABELS	
	Water-based Ink	Solvent Ink	Water-based Ink	Solvent Ink
Total ink used, (grams)	1,458.9	1,175.0	399.2	293.1
Ink solids retained on labels (grams)	609.8	609.8	152.1	152.1
Weight evaporated	849.1	565.2	247.1	141.0

Table 6. Weight loss data from laboratory evaporation at 70°C.

Material	Averages of triplicate runs				% Loss, Std Dev
	Initial wt.	Dry wt.	Wt. loss	% loss	
Black water based ink	12.17 gms	5.303	6.867	56.4	0.42
Green water based ink	12.05	5.04	7.01	58.2	0.21
Purple water based ink	12.22	4.66	7.56	61.9	0.20
Black alcohol based ink	15.38	7.99	7.39	48.1	0.60
Detergent cleaner	12.56	0.278	12.28	97.8	0.03

To estimate emissions that would have resulted from using solvent based inks, it was assumed that the same amount of solids would have been used for the printing of the labels as was used for the water-based inks. Then the total amount of ink that would have been used and the weight evaporated was calculated by using the percent loss factor determined in the laboratory (Table 6). Since less percentage of solvent-based ink was lost to evaporation, more solids per gram of ink would be applied to the labels than with the water-based ink. Thus, less total solvent-ink would be used and less total weight of component would be lost via evaporation. According to the operators at MPI Label Systems, they estimate that about

the same total amount of ink is required for a job for either type of ink. Thus, this analysis of emissions is conservative for the solvent-based ink. It should be noted that laboratory evaporation loss results given in Table 6 agree favorably with the total volatiles data given in the material safety data sheets (Table 2).

The next step is to estimate the weight of emissions of each specific component of the inks studied. These estimates are presented in Table 7. These estimates were made using the percent composition data from Table 2. For the water-based inks it was assumed that all of the alcohol, ammonia and amine evaporated and that the remainder of the loss was water.

Table 7. Amount of Component Emissions Estimated for each run and Type of Ink (grams)

Component	GREEN LABELS		PURPLE LABELS	
	Water-based Ink	Solvent Ink	Water-based Ink	Solvent Ink
Isopropyl alcohol	72.9	110.9	19.96	27.67
Ammonia	14.6	-	3.99	-
Dimethylethanol-amine	14.6	-	3.99	-
Water	747.0	-	219.16	-
Methyl alcohol	-	49.2	-	12.27
n-propyl alcohol	-	68.0	-	16.97
Ethyl alcohol	-	224.0	-	55.87
Ethyl acetate	-	44.0	-	10.97
VM&P naphtha	-	69.1	-	17.23
<b>TOTAL</b>	<b>849.1</b>	<b>565.2</b>	<b>247.1</b>	<b>141.0</b>

Liquid wastes were generated only during cleanup at the end of the press runs. These wastes were minimal and consisted of ink left in the pan and on the rollers, gaskets and plates at the end of the run after scraping and detergent cleaner. For the green run, 116.6 grams of ink remained in the pan. A total of 44.3 grams (about 44 milliliters) of cleaner was used. All of this was disposed of as waste water for a total of 160.9 grams. During the cleanup of the purple labels only 56.4 grams of liquid waste was produced. There was a more experienced operator for this run which resulted in less cleanup being required and less wastage.

During these two runs most of the ink retained on the fabric rags resulted from a spill that occurred during printing of the green labels. A total of 24.6 grams of ink was cleaned up as a result. These rags would have been sent to an industrial laundry for cleaning and reuse. Thus, this spilled ink would also result in a liquid waste.

### **ECONOMIC EVALUATION**

The approximate annual savings at MPI Label Systems as estimated by the plant manager is summarized in Table 8. They have observed no significant difference in costs between the two types of inks or cleaners being used. They can print on the same type of paper so there is also no difference in that regard. Although for most labels and paper stock the press speed with water-based inks can be increased about 10% over that with solvent-type inks, the economic impact of this slight increase in printing speed is difficult to quantify. At least the rate of printing can be slightly increased as a result of adopting the water-based inks. The company also reported that there is no difference to them in the cost of the printing plates.

The savings in waste disposal and handling results from the fact that the waste inks and cleaners no longer have to be disposed of as a hazardous waste, but can be released to the sanitary sewer. The other savings resulted from a reduced insurance rate when the company stopped using solvent-based inks and cleaners. The rationale was that the work environment was improved for the employees.

A significant off-setting factor is that the company decided to install a unit to treat its waste ink prior to discharge to the sewer. This filtration unit removes most of the color. The capital cost of that unit was about \$18,000. The colored absorbent is acceptable at the local municipal landfill. Since this treatment unit was not required as part of the change to water-based inks, its purchase and operating costs were not included in this analysis.

Table 8. Summary Economic Factors

COST COMPARISON FACTORS	
INKS	SAVINGS WITH WATER-BASED INKS
Raw materials	None
Printing speed	Approximately 10% faster
Waste disposal and handling	Minimum annual savings = \$10,000
CLEANERS	SAVINGS WITH AQUEOUS CLEANER
Raw materials	None
Disposal	Minimum annual savings = \$5,000
OVERALL	
Insurance liability	Approximately \$500/yr.
Inventory	None
Wiping materials	Annually at least \$1,000
<b>Total Annual Savings</b>	<b>At least \$16,500.</b>

#### DEGREE-OF-HAZARD ANALYSIS

The degree-of-hazard evaluations were conducted for three printing scenarios. The total mass of each scenario was set at 600 g/50,000 labels printed with a total usage of 1,000 gal or approximately 3,500 kg of material each. The large volume of material was necessary in order to conduct a degree-of-hazard analysis because of the RCRA Small Generator limit. The relevant analysis is the combined component equivalent toxic concentration for each printing type run.

- Scenario N° 1 employed solvent-based ink with solvent-based cleaner.
- Scenario N° 2 employed solvent-based ink with detergent cleaner.
- Scenario N° 3 employed water-based ink with detergent cleaner.

Table 9. Basis for Degree-of-Hazard Evaluation for Three Printing Scenarios

Component	Amount (%) of Ink or Cleaner	Total (g) per Scenario (600 g)	% of Total Scenario	Comments
<b>Solvent-Based Ink with Detergent Cleaner</b> Black Ink = 400 g + 200 g Cleaner/50,000 Labels Printed				
Polyamide Black	46.0	184.0	30.7	Considered as an innocuous toxic hazard <sup>16</sup> . Mr. Fishman, Sun Chemical Co. 201-365-3479.
Methyl alcohol	4.7	18.8	3.1	
Isopropyl alcohol	10.6	42.4	7.1	
N-propyl alcohol	6.5	26.0	4.3	
Ethyl alcohol	21.4	85.6	14.3	
Ethyl acetate	4.2	16.8	2.8	
VM&P naphtha	6.6	26.4	4.4	
<b>Solvent-Based Cleaner (200 g/50,000 Labels Printed)</b>				
Toluene	54.5	109.0	18.2	
Acetone	20.0	40.0	6.7	
Isopropyl alcohol	20.0	40.0	6.7	
Diacetone alcohol	5.5	11.0	0.9	
<b>Solvent-Based Ink with Detergent Cleaner</b> Black Ink = 400 g + 200 g Cleaner/50,000 Labels Printed				
Polyamide Black	46.0	184.0	30.7	
Methyl alcohol	4.7	18.8	3.1	
Isopropyl alcohol	10.6	42.4	7.1	
Ethyl alcohol	21.4	85.6	14.3	
N-propyl alcohol	6.5	26.0	4.3	
Ethyl acetate	4.2	16.8	2.8	
VM&P naphtha	6.6	26.4	4.4	
<b>Detergent Cleaner (200 g/50,000 Labels Printed)</b>				

Component	Amount (%) of Ink or Cleaner	Total (g) per Scenario (600 g)	% of Total Scenario	Comments
<b>Solvent-Based Ink with Detergent Cleaner</b> Black Ink = 400 g + 200 g Cleaner/50,000 Labels Printed				
Detergent cleaner	100.0	200.0	33.3	99.4% water plus 0.6% nonhazardous surfactants <sup>17</sup> (Union Carbide MP10) Mr. Dave Hostetler, ArrowChem, Inc. 800-438-5883
<b>Water-based Ink with Detergent Cleaner</b> Black Ink = 400 g + 200 g Cleaner/50,000 Labels Printed				
Ammonia	1.0	4.0	0.7	
Dimethylethanolamine	1.0	4.0	0.7	
Isopropyl alcohol	5.0	20.0	3.3	
Water	65.0	260.0	43.3	
Acrylic resin	20.0	80.0	13.3	LD <sub>50</sub> <5 g/kg <sup>18</sup> , Mr. Raleigh Turk 414-631-2443.
Azo pigments	8.0	32.0	3.3	LD <sub>50</sub> <5 g/kg <sup>18</sup>
<b>Detergent Cleaner (200 g/50,000 Labels Printed)</b>				
Detergent cleaner	100.0	200.0	33.3	99.4% water plus 0.6% nonhazardous surfactants (Union Carbide MP10) <sup>17</sup>

#### EQUIVALENT TOXIC CONCENTRATION MEASUREMENTS

The equivalent toxic concentration values of the solvent-based ink with the solvent-based cleaners, the solvent-base ink with water-based cleaner, and the water-based ink with the water-based cleaner are, 923, 121 and 347, respectively (Figure 3). The unexpected higher value for the water-based ink was due entirely to the oral toxicity of the ammonia used in the ink formulation.

This evaluation is for the bulk chemicals as they are received and assumes that the exposure is by ingestion. Thus, the results are most applicable to the liquid wastes that are generated as a result of printing

if there were no evaporative losses. If the ammonia is removed due to evaporation, the equivalent toxicity of the water-based ink and detergent cleaner would be about 20. The lowest concentration of ammonia in air at which any toxic effect to humans has been observed is 20 parts per million-

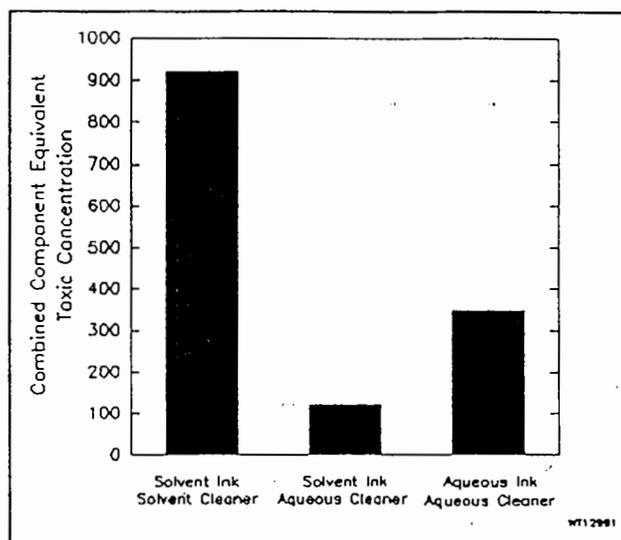
<sup>19</sup>. The effects noted were with the nose and

changes in trachea or bronchii. At MPI Label Systems, with ammonia in the water-based inks present at a concentration of 1 percent, and with the rapid changeover in the plant air, ammonia would be present in the air far below any measurable toxic effect.

By contrast, components of the solvent-based cleaner are much more toxic than the detergent cleaner. This can be seen by comparing the equivalent toxicity of the first scenario with the second in which the only difference is in the cleaners evaluated.

### CONCLUSIONS AND DISCUSSION

The change from solvent-based inks and cleaners to water-based ink and a detergent cleaner has resulted in less waste being generated at MPI Label Systems. This paper presents an in-plant quantitative measurement of the waste reduction benefits and trade-offs that have occurred. As with most changes in processes, the switch in materials, including changing the type of plate used, required many adjustments and fine-tuning. Also, in the past two years advances have been made in the water-ink formulation so they are easier to clean, and the rate at which labels can be printed has increased. The cooperative approach



**Figure 3** The combined component equivalent toxic concentration for the three printing scenarios.

between industry and government developed in this project, and the evaluation methods described can be used to evaluate the engineering and economic benefits of other similar chemical substitution projects.

The amount of solvent emissions to the air has been reduced per run by over 80 percent as a result of this change according to the measurements taken at MPI Label Systems. In addition, the components emitted are considerably less toxic to the press operators and the environment than was being emitted from the solvent-based inks. Since MPI Label Systems uses approximately 1,800 pounds of ink per year, an estimate can be made of the total weight of solvent emissions they currently release and what would be released if they were still using the solvent-based inks. This comparison is shown in Table 10 for MPI and the entire flexographic industry in the United States. For this estimate the laboratory evaporative loss percent for black ink as determined in this study was used. For the entire industry it has been reported that 300 million lbs/yr of water-based inks are currently required. Thus, at MPI Label Systems solvent emissions are estimated to have been reduced by over 800 lbs. per year. For the entire industry, almost 150 million pounds per year of toxic solvents are no longer emitted. Less air toxics are also released from the detergent cleaner than were released from the solvent cleaner previously used at MPI Label Systems.

Table 10. Comparative Solvent Loss to Air from Using Water-Based Inks

INK TYPE	MPI LABEL SYSTEMS, INC.	ENTIRE INDUSTRY
Solvent Inks	972 lbs/yr organic solvents	162,000,000 lbs/yr solvents
Water-based inks	126 lbs/yr	15,000,000 lbs/yr
<b>Total Solvent Reduction</b>	<b>846 lbs/yr</b>	<b>Approx. 147,000,000 lbs/yr</b>

Another benefit found is that hazardous wastes have been eliminated at MPI Label Systems. However, aqueous wash liquids discharged to the sanitary sewer have increased from essentially none to approximately 10,000 gallons per year.

Solid wastes generated in the form of wasted labels, wrap, trimmings and other paper has remained

about the same. In total, MPI estimates an annual cost savings of at least \$16,500 per year as a result of this change.

In addition to the above dollar advantages accruing from the use of water-based inks, and a relatively harmless cleaner, it is the opinion of the plant manager and his shop superintendent that the company is also realizing the following subjective benefits:

1. Water-based inks are easier to clean from pans, plates and rollers;
2. Waste inks is more easily disposed of;
3. Spilled ink is easier to clean up;
4. Waste going to a landfill is not classified as hazardous, giving MPI less long-term liability;
5. Expensive solvents are not required for cleanup; and
6. Employees are enjoying a cleaner, safer work environment.

An important lesson learned in this effort is the importance of agreeing on all planned plant tests with the company personnel to be involved. In our case we made it a point to closely monitor several label runs to learn the various steps, solutions, etc., to be encountered before collecting any in-plant measurements. However, by the time we were ready to take measurements, the plant had made changes in its operations. The operators prepared for a run the day before our arrival by completing preliminary tasks "to speed things up." Unfortunately, these well-meaning preparations short-circuited some of our measurements. As better materials appear, as less expensive procedures are noted -- but, mostly, if quality can be maintained or improved, and costs reduced, almost any process change will be considered.

During the planning stages of this project it was intended to quantitatively measure ink and cleaner usage at every step of the printing process. After a preliminary run it became apparent that several of these measurements would be very difficult to carry out. Two examples are worth noting. First, we intended to determine by weighing the amount of dry ink actually deposited on labels ( $Q$  in equation 1). This was to be accomplished by weighing approximately 1000 blank labels as they came from the press, and 1000 printed labels. After numerous measurements, at least for the labels we measured, it became

obvious that the amount of ink on anything but a very large number of labels is negligible. It appears that variations in the paper weight and perhaps amount of adhesive are much greater than the amount of ink applied. Second, we intended initially to measure the amount of ink wasted on the paper trimmed from around each label. The trimmed top layer is peeled away from its paper backing, then collected as a roll of waste. It was not possible to separate one layer of these trimmings from another.

The result of these two experiences was that we decided to simply weigh the ink reservoir before and after a run and consider the difference due to all ink uses - labels, trim waste, spills, cleanup of the ink pans, rollers and printing plates. With the exception of the ink lost during cleanup (and on a relatively short run this will represent most of the ink used) the balance will have its solvents lost to the shop air.

It should be kept in mind that the scope of this evaluation was limited in several important aspects. First, the image and plate making steps were not included in this evaluation of waste produced. As mentioned earlier, the plates used at the MPI Label Systems plant evaluated were produced by another company. The wastes generated in formulating the inks and cleaners were not comparatively evaluated in this study. It could be possible that the reduction in waste produced during the printing operation is more than offset by increased waste produced during ink or cleaner manufacturing. This seems unlikely since the solvent components of both materials currently being used are much less than the solvent-based materials. Finally, the impact of using water-based inks on the recyclability of the product labels was not evaluated. Since these labels are placed on many types of products, they will generally not be recycled as waste paper.

MPI Label Systems and the entire flexographic printing industry has benefited economically, technically and in the physical well-being of its employees by changing from solvent-based to water-based inks and cleaners. The environment has also benefited. Additional benefits will be realized as the use of solvent-type industrial cleaners is eliminated. Label customers are also benefiting from the change in technology with better quality labels.

## ACKNOWLEDGMENT

This work was accomplished in large part because of generous cooperation by MPI Label Systems, University Park, Illinois, Water Technologies, Inc., Iron Station, North Carolina, BASF Corp., Chicago, Illinois, and the Flexographic Technical Association, Ronkonkoma, New York. The work was performed jointly by the USEPA and the Hazardous Waste Research and Information Center, Illinois Dept. of Energy and Natural Resources, Champaign, Illinois, under cooperative agreement CR-815829-01-0.

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## THE TREATABILITY OF URBAN STORMWATER TOXICANTS

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### ABSTRACT

This paper summarizes some of the information obtained during a research project sponsored and directed by the EPA's Storm and Combined Sewer Research Program and conducted under a subcontract from Foster-Wheeler/Enviresponse. Earlier research, that was reported at last year's Sixteenth Annual Hazardous Waste Research Symposium, investigated typical toxicant concentrations in stormwater, the origins of the toxicants found, and rain and land use factors that influenced the toxicant concentrations. The most recent research, which is summarized in this paper, investigated the control of stormwater toxicants through conventional treatment unit processes.

Twelve sheetflow samples were collected from the source areas that were found previously to generally produce the most toxic runoff waters. These areas were automobile service areas (gas stations, car washes, oil change and other automobile maintenance facilities), industrial parking and loading dock areas, and automobile salvage yards. These samples were subjected to a variety of treatment processes. The bench scale treatability tests included settling columns, sieving screens, membrane filters, aeration, photo-degradation, aeration and photo-degradation combined, floatation, and alum addition. Toxicity changes were monitored using the Microtox bioassay test. The Microtox test was extensively compared to conventional bioassay and chemical tests during previous research phases.

The benefits of the treatment processes varied for the different samples. However, some of the treatment processes consistently provided the greatest toxicity reductions. The most beneficial treatment tests included settling for at least 24 hours (generally 40 to 90% reductions), screening through at least 40 micron screens (20 to 70% reductions), and aeration and/or photo-degradation for at least 24 hours (up to 80% reductions). The floatation tests produced floating sample layers that generally increased in toxicity with time and lower sample layers that generally decreased in toxicity with time. However, the benefits were quite small (less than 30% reduction). Alum additions substantially reduced the turbidity of the samples. but the changes in toxicity were highly irregular.

The next project phases will include more extensive laboratory and field tests, using prototype treatment designs based on these initial bench scale tests.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

### BACKGROUND

Urban stormwater runoff has been identified as a major contributor to the degradation of many urban streams and rivers (1 - 4). Organic and metallic toxicants are expected to be responsible for much of these detrimental effects, and have been found in urban runoff discharges during many previous studies (5 - 8).

All U.S. cities having populations greater than 100,000 (which total about 15,000 square miles) (9) will be required to participate in the EPA's stormwater permit program (Federal Register, November 16, 1990). The Nationwide Urban Runoff Program (NURP) monitored toxicant discharges from 28 cities (5). Based on this monitoring, it is expected that these large cities are responsible for substantial toxicant discharges that directly enter the nation's surface receiving waters from stormwater outfalls. This limited NURP data was collected mostly from residential areas, with some commercial areas represented. More recent information indicates that industrial stormwater discharges can have many times the concentrations of the toxicants as the areas represented in the NURP data (10). In addition, base flows occurring in storm drains during dry weather that may be contaminated by non-stormwater discharges (such as industrial waste cross-connections), can also significantly increase these estimated loadings (11). The EPA sponsored research summarized in this paper was conducted to obtain much needed information concerning the sources and potential control of these stormwater toxicants.

### FIRST RESEARCH PHASE SUMMARY

The first phase of this research included the collection and analysis of about 150 urban stormwater runoff and combined sewer overflow (SCSO) samples from a variety of source areas and under different rain conditions. A number of combined sewer overflow and detention pond samples were also evaluated. This effort was significantly greater than had been attempted previously for toxic pollutants in stormwater.

Samples were analyzed for many organic pollutants using two gas chromatographs, one with a mass selective detector (GC/MSD) and another with an electron capture detector (GC/ECD), and for metals using a graphite furnace equipped atomic absorption spectrophotometer (GFAA). All samples were further analyzed for particle size distributions (from about 1 to 100 microns) and for toxicity using the Microtox (from Microbics) toxicity screening technique. All samples were also filtered to determine the liquid/solid partition coefficients of the pollutants and the relative toxicities of the filterable and nonfilterable portions of the samples. Overall, about 300 sample components (filterable and total portions of 150 samples) were analyzed to determine toxicant concentrations in sheetflows and other SCSOs as part of the first phase of this project. The following paragraphs briefly summarize the first project phase results (from ref. 8).

Most pH values were in a narrow range of 7.0 to 8.5 and the suspended solids concentrations were generally less than 100 mg/L. The particle size ranges were usually narrow for any one sample, but the distribution ranges developed using all samples from a single source area category were substantially greater.

Only a small fraction of the toxic organic pollutants analyzed were frequently detected. Thirteen organics were detected in more than ten percent of all samples analyzed. The greatest detection frequencies were for 1,3-dichlorobenzene and fluoranthene, which each had detection frequencies of 23 percent. The organics most frequently found in these samples were similar to the organics most frequently detected at outfalls in prior studies

(such as during the NURP study, ref. 5). The PAHs, especially fluoranthenes and pyrenes were the most commonly detected organic compounds.

The organic compounds analyzed had the greatest frequencies of detection in roof runoff, urban creeks, and CSO samples. Vehicle service areas and parking areas had several of the observed maximum organic compound concentrations observed. Most of the organics were associated with nonfilterable sample portions.

In contrast to the organics, the heavy metals were detected in almost all samples analyzed, including the filtered samples. Roof runoff had the highest observed concentrations of zinc, probably due to galvanized roof drainage components. Parking areas had the highest nickel concentrations, while vehicle service areas had the highest concentrations of cadmium and lead. Urban creek samples had the highest copper concentrations, probably due to illicit discharges.

About 15 percent of all of the unfiltered samples analyzed were considered highly toxic using the Microtox screening procedure. The remaining samples were approximately evenly split between being moderately toxic and not being toxic. The Microtox screening tests found that CSOs had the greatest percentage of samples considered the most toxic, followed by samples obtained from parking and industrial storage areas. Runoff from paved areas all had relatively low suspended solids concentrations and turbidities, especially compared to samples obtained from unpaved areas.

Preliminary data evaluations indicated that variations in observed Microtox toxicities and organic toxicant concentrations may be greater for different rains than for the different source areas sampled. As an example, high concentrations of PAHs were mostly associated with long-antecedent dry-periods.

The literature review conducted during the first project phase found that many processes will affect the potential transport and fate mechanisms of these pollutants. Sedimentation in the receiving water is the most common fate mechanism because many of the pollutants investigated are mostly associated with particulate matter. Exceptions included zinc and 1,3-dichlorobenzene which were mostly associated with the filterable sample portions. Particulate removal can occur in many SCSO control facilities, including catchbasins, swirl concentrators, screens, drainage systems, and detention ponds. These control facilities allow removal of the accumulated polluted sediment for final disposal in an appropriate manner. Uncontrolled sedimentation will occur in receiving waters, such as lakes, reservoirs, or large rivers. In these cases, the wide dispersal of the contaminated sediment is difficult to remove and can cause significant detrimental effects. Biological or chemical degradation of the toxicants in the sediments may occur, but is quite slow for many of the pollutants in the expected anaerobic environments. Degradation of the soluble pollutants in the water column may also occur, especially when near the surface in aerated waters. Volatilization (evaporation) is also a mechanism that may affect many of the detected organic toxicants. Increased turbulence and oxygen supplies would encourage these processes that may significantly reduce pollutant concentrations. Sorption of pollutants onto suspended solids and metal precipitation increases the sedimentation potential of the pollutants and also encourages more efficient bonding of the pollutants in soils, preventing their leaching to surrounding waters.

The second project phase, summarized below, examined the usefulness of a variety of treatment unit processes that were expected to reduce the toxicities found in the initial project phase. Later project phases will examine the treatability of SCSO toxicants in greater detail, especially in terms of making and testing modifications to existing treatment processes.

## METHODOLOGY

### SAMPLING EFFORT AND EXPERIMENTAL ERROR

The relative importance of different source areas (such as roofs, streets, parking areas, etc.) in contributing toxicants was determined from the first project phase activities that examined 150 source area

samples (8). These previous samples were collected from the most significant potential toxic pollutant source areas in residential, commercial, and industrial land uses. The areas that received the most sampling attention during both project phases were parking and storage areas in industrial and commercial areas. These areas had been noted in previous studies to have the largest potential of discharging toxicants (10). Sheetflow samples were collected during five Birmingham Alabama rains. Replicate samples taken from many of the same source areas, but during different rains, enabled differences due to rain conditions versus site locations to be statistically evaluated.

The second research phase included extensive analyses of 12 samples. Table 1 lists these samples, including their sampling dates and source area categories. These samples represent practically all of the rains that have occurred in the Birmingham area since the second project phase field activities were able to begin in June, 1990. Information is also shown concerning the toxicities of the samples before treatment. These independent replicates were used to measure the measurement errors associated with the Microtox procedure. The means, standard deviations, and relative standard deviations (standard deviation divided by the mean, times 100) of the replicate toxicity values are also shown on Table 1. The number of analyses refer to the total number of Microtox analyses that were conducted for all of the treatability tests for each sample.

The initial toxicity values were plotted on normal-probability plots to indicate their probability distributions. Almost all of the samples had initial toxicity values that were shown to be normally distributed. Therefore, the relative standard deviation values shown on Table 1 can be used as an indication of the confidence intervals of the Microtox measurements. The relative standard deviations ranged from 2.3 to 9.8 percent, with an average value of 5.1 percent. Therefore, the 95 percent confidence interval for the Microtox procedure ranged between 5 and 20 percent, and averaged about 10 percent (two times the relative standard deviation values include 95.4 percent of the values, if normally distributed). These confidence intervals are quite narrow for a bioassay test and indicate the good repeatability of the procedure. One of the important factors of the Microtox test is the use of a very large number of organisms (about one million) for each analysis, reducing erratic test responses that may be caused by unusual individual organisms. In all cases, statistical tests were performed on the test results to indicate the significance of the different treatability tests.

Figure 1 contains box plots of the initial toxicity values (18). These indicate the spread of toxicity values that were represented by the samples. Two samples (B and D) were found to be highly toxic, while the remainder were moderately toxic.

## SAMPLING PROCEDURES

The sheetflow samples were collected using manual grab procedures. For deep sheetflows, samples were collected directly into the sample bottles, or dipped using glass beakers. For shallow sheetflows, hand operated pumps created a vacuum in the sample bottle which then drew the sample directly into the container through Teflon tubes. About ten to twenty liters of each sample were collected for the treatability analyses. The samples were all obtained from the Birmingham, Alabama area.

## TOXICITY SCREENING TESTS

A number of previous studies have found high concentrations of toxic pollutants in stormwater samples (as summarized in ref. 4). Some urban stormwater runoff studies attempted to use conventional 96-hr fathead minnow fish bioassay toxicity tests (such as in ref.12), but very few fish died during the tests. However, in situ taxonomic studies of urban runoff receiving waters found significant evidence of toxic effects from the long-term exposure to these pollutants (such as reported in ref. 2, for the same stream as the negative fish bioassay tests). More recent bioassay tests have used more sensitive organisms and have detected significant SCSO toxicities (ref.13, from Syracuse, NY; ref. 14 from Birmingham, AL; ref. 15 from Waterbury, CN; and ref. 16 from San Francisco Bay, CA).

The objective of this toxicity monitoring task was to obtain toxicity measurements from a large number of subsamples obtained during different stages of bench scale treatment tests. These tests were not used to determine the absolute toxicities of the samples, but only to examine the toxicity differences between the sample partitions from different treatment tests. To evaluate the different treatment options, it was necessary to use a rapid screening method that only used small sample volumes. The toxicity testing procedure that was used (Microtox from Microbics, Inc.) uses luminescent microorganisms to indicate relative toxicities of samples. A series of special tests were made during the first project phase to compare the toxicities of about 20 selected sheetflow and CSO samples to both the Microtox screening method and conventional bioassay methods.

The toxicity, as determined by the Microtox procedure, was expressed as three values,  $I_{10}$  (the percentage light decrease after 10 minutes of exposure),  $I_{35}$  (the percentage light decrease after 35 minutes of exposure), and the  $EC_{50}$ . The  $EC_{50}$  is the sample dilution corresponding to a 50 percent light decrease after a 35 minute exposure. Therefore, only samples that have  $I_{35}$  values greater than 50 were further tested to determine the  $EC_{50}$  values. Higher values of  $I_{10}$  and  $I_{35}$ , and lower fractions of  $EC_{50}$ , correspond to greater toxicities.

Microbics suggests that light decrease values greater than 60 percent correspond to "highly" toxic samples, light decrease values between 20 and 60 percent correspond to "moderately" toxic samples, and light decrease values less than 20 percent correspond to "not" toxic samples.

During the first project phase, a number of special tests were conducted that examined problems associated with sample storage time, preservation, and sample containers. Teflon and glass were exclusively used to reduce the effects of the containers on the sample toxicities and samples were all examined within 24 hours of sample collection. Samples were also stored at 3° C to 5° C.

#### PARTICLE SIZE ANALYSES

Most SCSO physical treatment removal efficiencies significantly relate to the particle size distributions and settling velocities of solids (17). Wet detention ponds, catchbasins, grass filters, street cleaning, microscreening, filtration, and swirl concentrators are some of the pollutant control methods that require a knowledge of particle size and/or settling characteristics. Additionally, the fates of many toxic pollutants in receiving waters are also very sensitive to the physical characteristics of particles. It is not possible to correctly design many of these physical treatment devices without knowing the specific particle size distributions and settling velocities of the SCSOs.

A laser particle counter (SPC-510 from Spectrex Corp.) was used to analyze particle size distributions for all of the samples during the different treatment phases. This instrument produces particle size distribution plots for particle sizes ranging from 0.5 microns to more than 100 microns. Settling column tests were also concurrently conducted during this research phase to determine the specific gravities and settling velocities of SCSO samples.

#### SOLIDS AND TURBIDITY ANALYSES

Nephelometric turbidity analyses were conducted for all subsamples during the treatability tests, using EPA method 180.1. Gravimetric solids analyses were conducted on all settling column subsamples to calculate settling rates and specific gravity. EPA method 160 was used for these solids analyses.

## TREATABILITY TESTS

Phase 2 included tests to examine the treatability of source area samples. As noted above, the samples were all relatively toxic. This has allowed a wide range of laboratory partitioning and treatability analyses to be conducted without having detection limit problems. The following tests were used for this study:

- o Settling column (a 1.5 inch by 30 inch Teflon column)
- o Floatation (a series of eight narrow neck glass 100 mL volumetric flasks)
- o Screening and filtering (a series of eleven stainless steel sieves, from 20 to 106 microns, plus a 0.45 micron membrane filter)
- o Photo-degradation (a two liter glass beaker with a 60 W "grow light" incandescent light placed 6 inches above the water, stirred with a magnetic stirrer, temperature of water and evaporation rate also monitored)
- o Aeration (the same beaker arrangement as above, without the grow light, but with filtered compressed air keeping the test solution supersaturated and well mixed)
- o Photo-degradation and aeration combined (the same beaker arrangement as above, with compressed air, grow light, and stirrer)
- o Chemical addition (a standard glass jar tests using alum and 800 mL samples)
- o Undisturbed control sample (a sealed and covered glass jar at room temperature)

These bench scale tests were all designed to use small sample volumes because of the difficulty of obtaining large sample volumes from many of the source areas that were to be examined.

Each test (except the filtration and chemical addition tests) was conducted over a period of time. Subsamples were typically obtained for toxicity analyses at the following time intervals during the tests: 0, 1, 2, 3, 6, 12, 24, 48, and 72 hours. In addition, settling column samples were also obtained at many times within the first hour: 1, 3, 5, 10, 15, 25, and 40 minutes. The chemical addition tests were conducted using alum at several concentrations in a standard jar test. In addition to the Microtox toxicity tests, most samples were analyzed for turbidity and particle sizes. All settling column samples were also analyzed for gravimetric suspended solids content to enable calculations of settling velocity to be made.

Future project phases will include pilot- and full-scale tests of various control and treatment practices. Especially important in the future project phases will be the testing of modifications to conventional stormwater and CSO treatment processes and the design and testing of combination treatment systems suitable for small source areas (such as pavement at automobile service facilities, especially gas stations).

## DATA OBSERVATIONS

The Microtox procedure allowed toxicity screening tests to be conducted on each sample partition during the treatment tests. This efficient procedure enabled more than 900 toxicity tests (and turbidity and particle size distribution tests) to be made.

Figures 2 through 10 are plots of the toxicity reductions observed during these tests. Each of these figures contains the data for one of the treatment tests conducted, including the control test. Each figure contains three plots, one contains the treatment responses for the automobile service facility samples (samples B, C, E, and H), another for the industrial loading and parking area samples (samples D, F, G, I, J, and K), and the last one for the automobile salvage yard samples (samples L and M). Even though the data are plotted into these three groups, very few consistent differences are noted in the way the samples responded to the treatments. As expected, there are greater apparent differences between the treatment methods than between the sample groupings. Statistical tests that will be conducted during the current project phase will examine these groupings in detail.

These initial data plots show the percentage reduction of toxicity, as measured by the Microtox procedure. It is expected that some of the treatment processes will have varying effects, depending on the initial toxicity values, which were shown to vary considerably. Other future statistical tests will therefore also examine the effects of these treatment schemes on samples having different initial toxicities.

Tables 2 through 4 summarize results from the non parametric Wilcoxon signed ranks test (using SYSTAT: The System for Statistics, Version 5, SYSTAT, Inc., Evanston, Ill.) for different treatment combinations. This statistical test indicates the two-sided probabilities that the sample groups are the same. A probability of 0.05, or less, is used here to indicate significant differences in the data sets. As an example, Table 3 indicates that for sample D, the undisturbed control sample was significantly different (with probabilities of 0.02) compared to all of the treatment tests.

The aeration test provided the most samples that had significant probabilities of being different from the control condition. Settling, photo-degradation, and aeration and photo-degradation combined, were tied in providing the next greatest number of samples that had significant probabilities of being different from the control condition. The floatation test had many samples that had significant differences in toxicity of the top floating layer compared to the control sample. However, the more important contrast between the middle sample layers (below the top floating layer) and the control sample, which would indicate a reduction in toxicity of post-treated water, had very few samples that were significantly different from the control sample.

The absolute magnitudes of toxicity reductions must also be considered. As an example, it may be significant, but unimportant, if a treatment test provided many (and therefore consistent) samples having significant differences compared to the control sample, if the toxicity reductions realized were very small.

## CONCLUSIONS

As shown on Figures 2 through 10, good separation of toxicant responses were found during many of the treatment tests. The most beneficial treatment tests included settling for at least 24 hours (providing generally 40 to 90% reductions), screening through at least 40 micron screens (20 to 70% reductions), and aeration and/or photo-degradation for at least 24 hours (up to 80% reductions). Increased settling, aeration or photo-degradation times, and screening through finer meshes, all resulted in greater toxicity reductions. The floatation tests produced floating sample layers that generally increased in toxicity with time and lower sample layers that generally decreased in toxicity with time. However, the benefits were quite small (less than 30% reduction). Alum additions substantially reduced the turbidity of the samples, but the changes in toxicity were highly irregular. These results, in conjunction with results from the first project phase, will enable us to modify treatment designs to optimize toxicant removals from critical stormwater runoff source areas.

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TABLE 1. SAMPLE DESCRIPTIONS

Automobile Service Area Samples:

Sample	Date	Toxicity (% light reduction)	Number of Analyses	Standard Deviation	Relative Standard Deviation (percent)
B	7/10/90	78	28	7.6	9.8
C	7/21/90	34	42	2.9	8.5
E	8/19/90	43	74	1.3	3
H	10/17/90	50	88	1.5	3

Industrial Loading and Parking Area Samples:

Sample	Date	Toxicity (% light reduction)	Number of Analyses	Standard Deviation	Relative Standard Deviation (percent)
D	8/2/90	67	74	2.1	3.1
F	9/12/90	31	88	1.5	4.9
G	10/3/90	53	88	3	5.7
I	10/24/90	55	89	1.9	3.4
J	11/5/90	49	89	1.1	2.3
K	11/9/90	28	89	2.2	8.1

Automobile Salvage Yard Samples:

Sample	Date	Toxicity (% light reduction)	Number of Analyses	Standard Deviation	Relative Standard Deviation (percent)
L	11/28/90	26	89	1.4	5.5
M	12/3/90	54	89	1.8	3.4
	minimum:	26		1.1	2.3
	maximum:	78		7.6	9.8
	mean:	47		2.4	5.1
	st. dev.:	16			
	total:		927		

TABLE 2. TWO-SIDED PROBABILITIES COMPARING DIFFERENT TREATMENT TESTS FOR AUTOMOBILE SERVICE AREA SAMPLES (1)

Automobile Service Areas Samples:				
Undisturbed versus:	B	C	E	H
settling	n/a	0.25	0.02	0.41
aeration	n/a	0.31	0.25	0.07
photo-degradation	n/a	0.12	0.06	0.16
aeration and photo-degrad.	n/a	0.35	0.24	0.06
floatation - top layer	n/a	n/a	0.74	0.02
floatation - middle layer	n/a	n/a	0.31	0.87
Aeration and Photo-degradation:				
aeration vs. photo-degrad.	0.23	0.02	0.49	0.08
aeration vs. aeration and photo.	n/a	0.03	0.99	0.14
photo vs. aeration and photo.	n/a	0.25	0.14	0.02
Floatation:				
top layer vs. middle layer	n/a	n/a	0.49	0.01
Settling versus:				
aeration	0.46	0.02	0.02	0.45
photo-degradation	0.12	0.25	0.02	0.79
aeration and photo-degradation	n/a	0.61	0.02	0.09
floatation - top layer	n/a	n/a	0.02	0.05
floatation - middle layer	n/a	n/a	0.02	0.09
Aeration versus:				
floatation - top layer	n/a	n/a	0.39	0.02
floatation - middle layer	n/a	n/a	0.21	0.02
Photo-Degradation versus:				
floatation - top layer	n/a	n/a	0.18	0.02
floatation - middle layer	n/a	n/a	0.03	0.02
Aeration and Photo-Degradation versus:				
floatation - top layer	n/a	n/a	0.49	0.02
floatation - middle layer	n/a	n/a	0.04	0.02

(1) Probabilities were calculated using the Wilcoxon signed-rank test for paired data sets. Comparisons having probabilities less than, or equal to, 0.05 are considered significantly different.

TABLE 3. TWO-SIDED PROBABILITIES COMPARING DIFFERENT TREATMENT TESTS FOR INDUSTRIAL LOADING AND PARKING AREA SAMPLES (1)

	Industrial Loading and Parking Area Samples:					
	D	F	G	I	J	K
Undisturbed versus:						
settling	0.02	0.12	0.09	0.07	0.01	0.01
aeration	0.02	0.05	0.06	0.04	0.01	0.01
photo-degradation	0.02	0.04	0.03	0.07	0.01	0.01
aeration and photo-degrad.	0.02	0.05	0.03	0.09	0.01	0.01
floatation - top layer	0.02	0.05	0.13	0.01	0.03	0.21
floatation - middle layer	0.02	0.78	0.02	0.26	0.16	0.17
Aeration and Photo-degradation:						
aeration vs. photo-degrad.	0.21	0.24	0.74	0.01	0.04	0.05
aeration vs. aeration and photo.	0.61	0.18	0.04	0.01	0.11	0.51
photo vs. aeration and photo.	0.21	0.16	0.25	0.79	0.74	0.12
Floatation:						
top layer vs. middle layer	0.72	0.41	0.05	0.02	0.07	0.12
Settling versus:						
aeration	0.18	0.33	0.61	0.48	0.41	0.02
photo-degradation	0.02	0.78	0.61	0.06	0.12	0.02
aeration and photo-degradation	0.03	0.67	0.75	0.05	0.12	0.03
floatation - top layer	0.14	0.05	0.13	0.04	0.01	0.02
floatation - middle layer	0.72	0.09	0.31	0.05	0.02	0.01
Aeration versus:						
floatation - top layer	0.39	0.04	0.09	0.02	0.01	0.09
floatation - middle layer	0.12	0.09	0.18	0.03	0.01	0.01
Photo-Degradation versus:						
floatation - top layer	0.04	0.04	0.04	0.02	0.01	0.09
floatation - middle layer	0.04	0.05	0.24	0.04	0.01	0.01
Aeration and Photo-Degradation versus:						
floatation - top layer	0.03	0.04	0.06	0.02	0.01	0.05
floatation - middle layer	0.18	0.21	0.04	0.04	0.01	0.01

(1) Probabilities were calculated using the Wilcoxon signed-rank test for paired data sets. Comparisons having probabilities less than, or equal to, 0.05 are considered significantly different.

TABLE 4 TWO-SIDED PROBABILITIES COMPARING DIFFERENT TREATMENT TESTS FOR AUTOMOBILE SALVAGE YARD SAMPLES (1)

	Automobile Salvage Yard Samples:	
	L	M
Undisturbed versus:		
settling	0.02	0.02
aeration	0.02	0.03
photo-degradation	0.02	0.16
aeration and photo-degrad.	0.02	0.09
floatation - top layer	0.01	0.09
floatation - middle layer	0.59	0.89
Aeration and Photo-degradation:		
aeration vs. photo-degrad.	0.08	0.01
aeration vs. aeration and photo.	0.07	0.08
photo vs. aeration and photo.	0.99	0.14
Floatation:		
top layer vs. middle layer	0.02	0.07
Settling versus:		
aeration	0.02	0.12
photo-degradation	0.02	0.01
aeration and photo-degradation	0.02	0.02
floatation - top layer	0.02	0.02
floatation - middle layer	0.02	0.03
Aeration versus:		
floatation - top layer	0.02	0.01
floatation - middle layer	0.02	0.01
Photo-Degradation versus:		
floatation - top layer	0.02	0.03
floatation - middle layer	0.02	0.21
Aeration and Photo-Degradation versus:		
floatation - top layer	0.02	0.01
floatation - middle layer	0.02	0.16

(1) Probabilities were calculated using the Wilcoxon signed-rank test for paired data sets. Comparisons having probabilities less than, or equal to, 0.05 are considered significantly different.

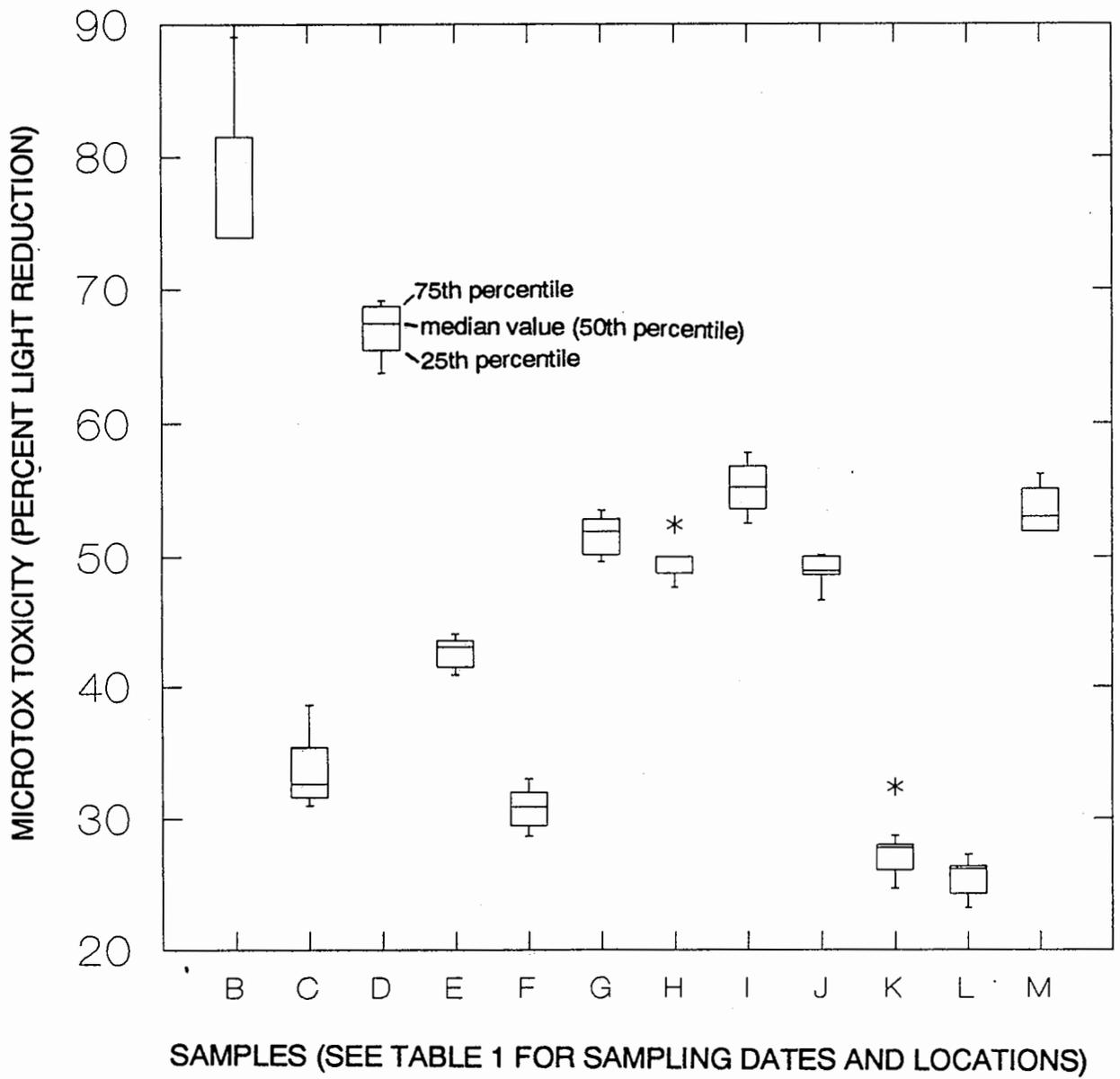


Figure 1. Box plot of initial sample Microtox toxicities (ref. 18).

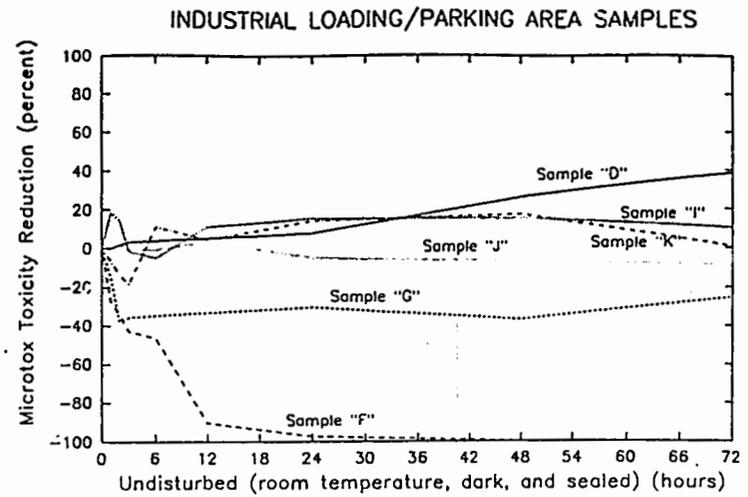
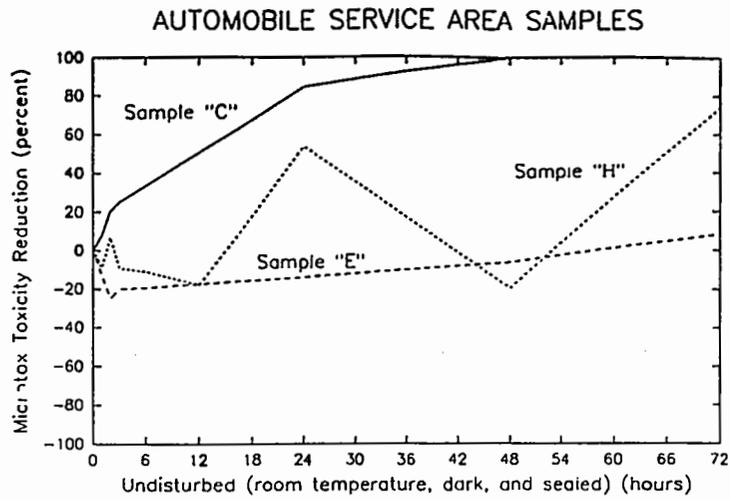
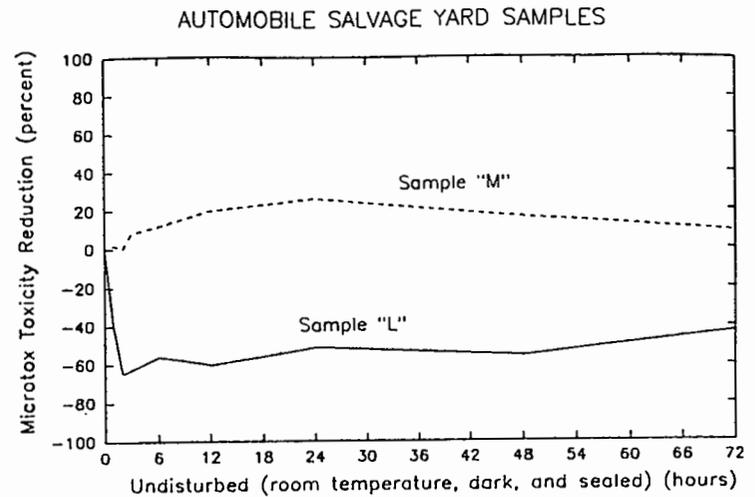
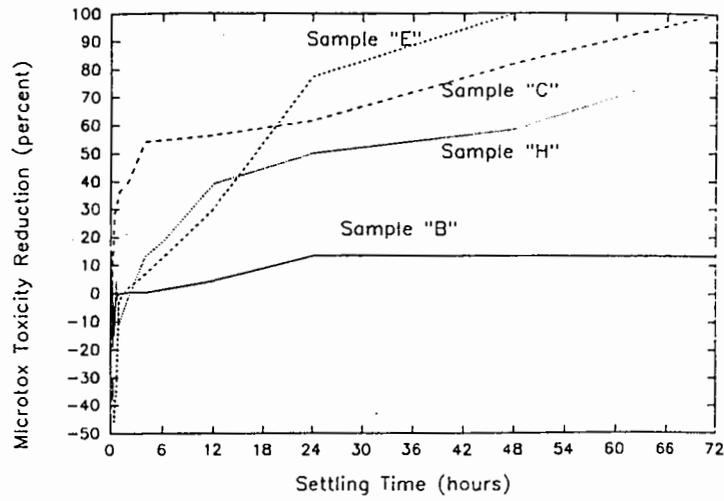


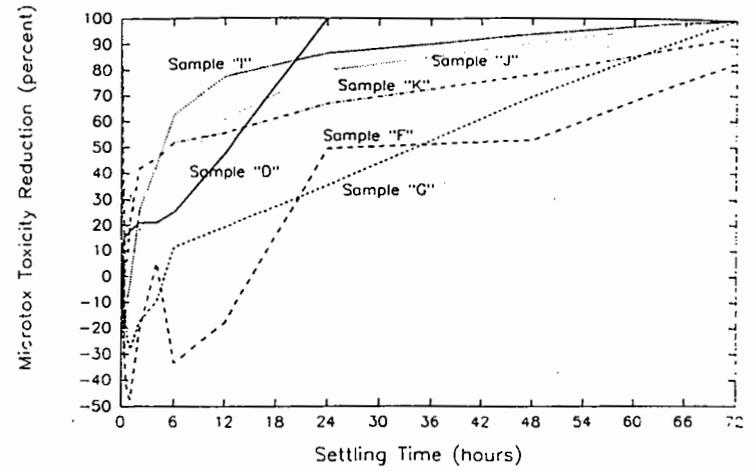
Figure 2. Undisturbed sample toxicity trends.



AUTOMOBILE SERVICE FACILITY SAMPLES



INDUSTRIAL LOADING/PARKING AREAS



AUTOMOBILE SALVAGE YARD SAMPLES

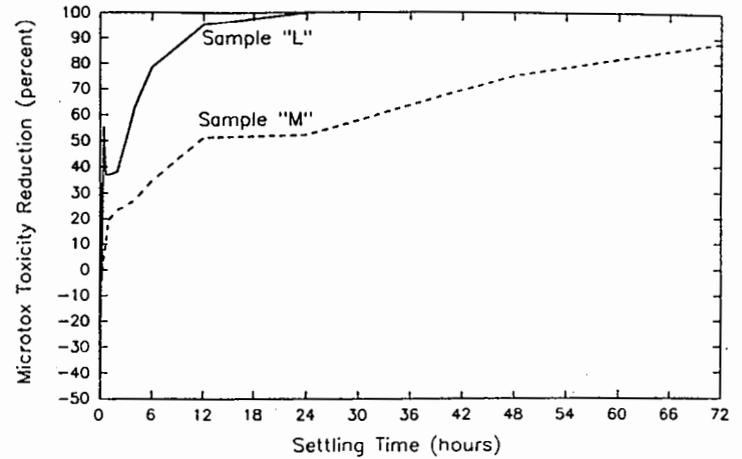


Figure 3. Settling column treatability test toxicity trends.

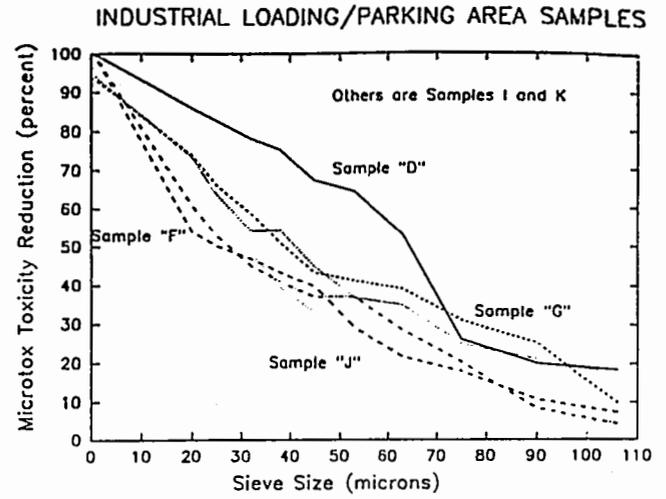
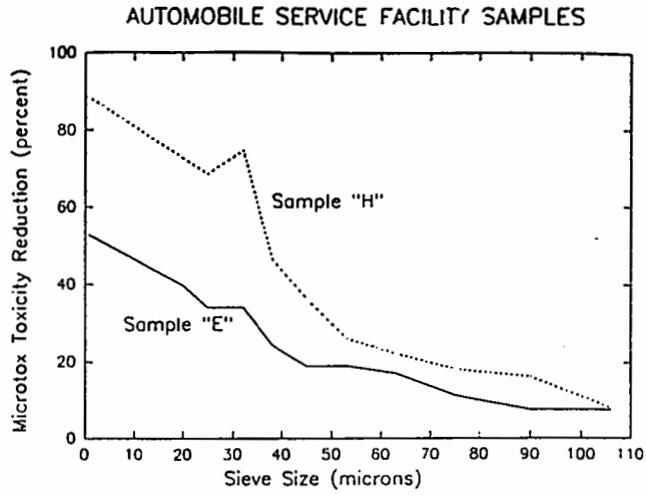
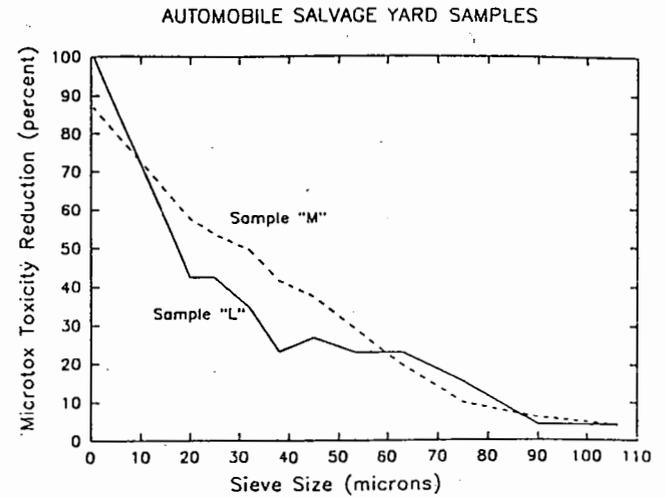


Figure 4. Sieve treatability test toxicity trends.



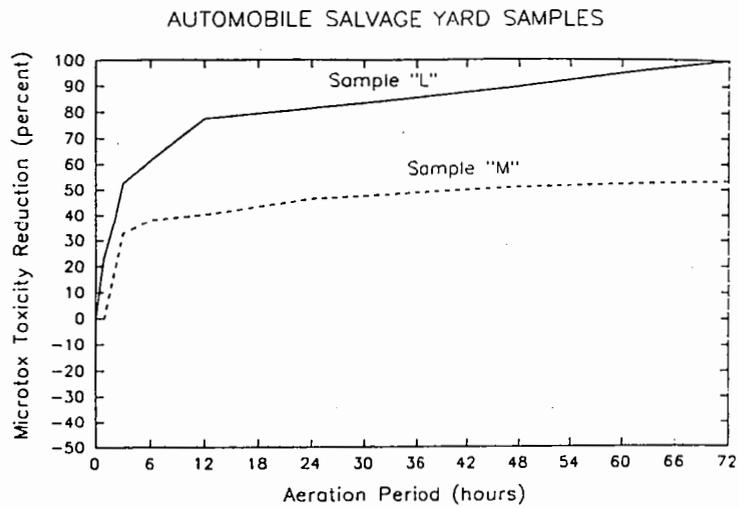
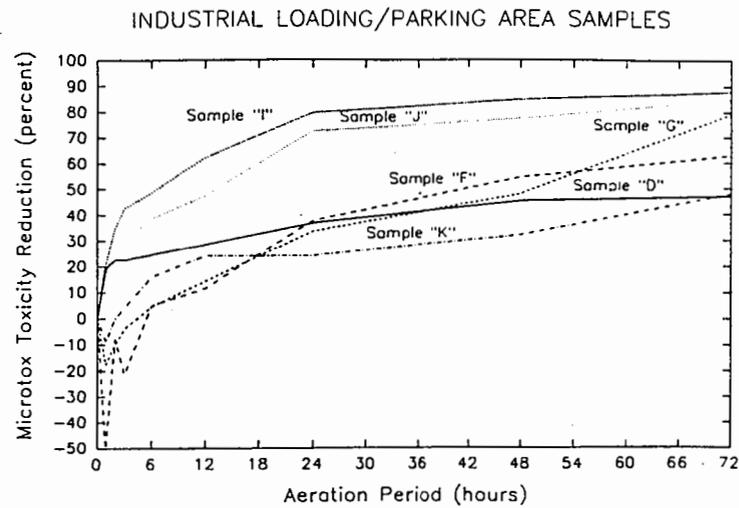
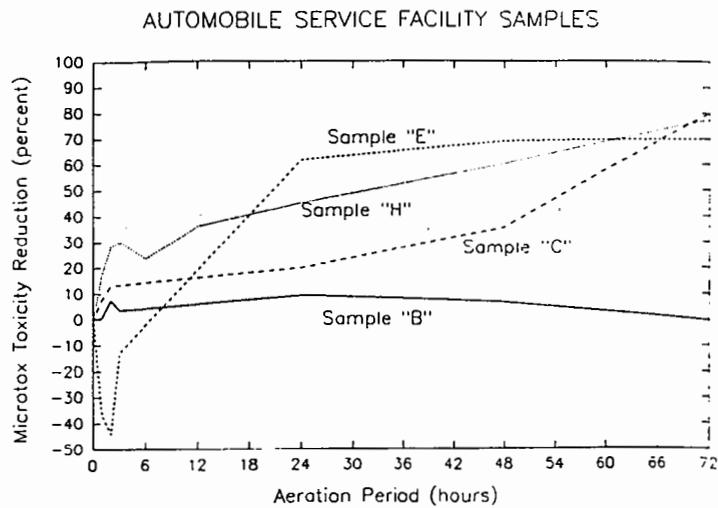


Figure 5. Aeration treatability test toxicity trends.

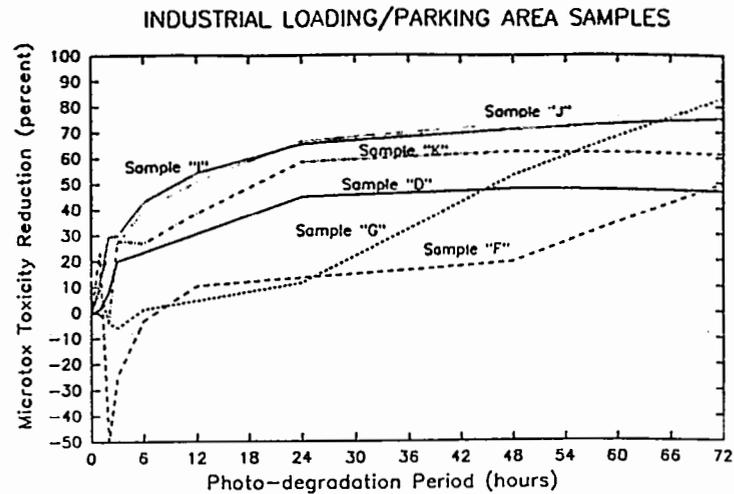
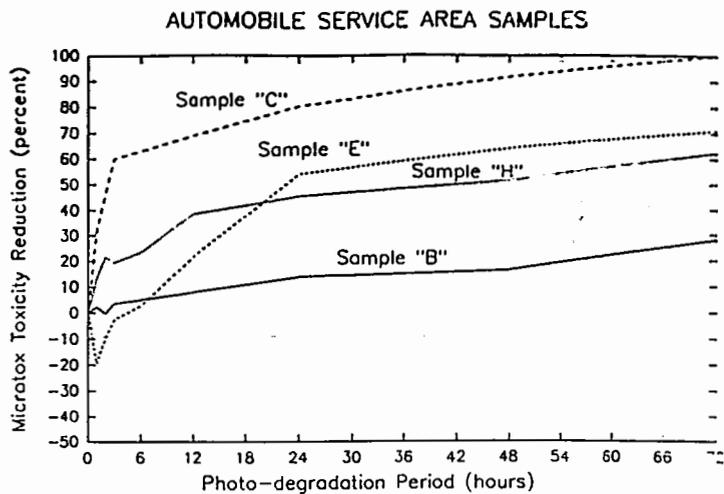
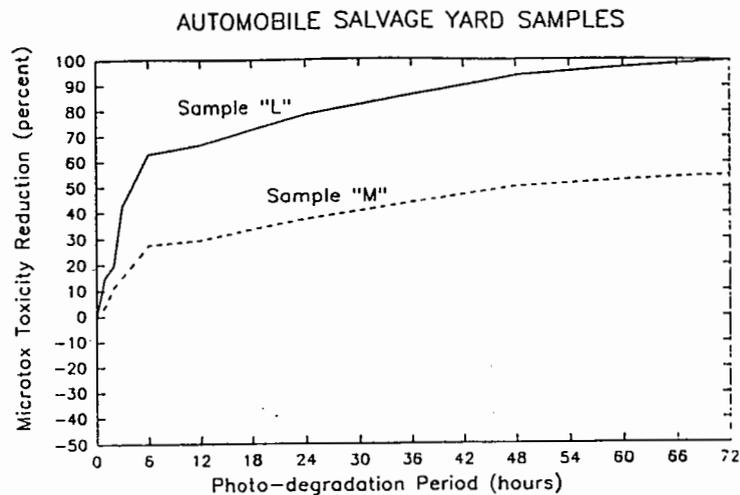


Figure 6. Photo-degradation treatability test toxicity trends.



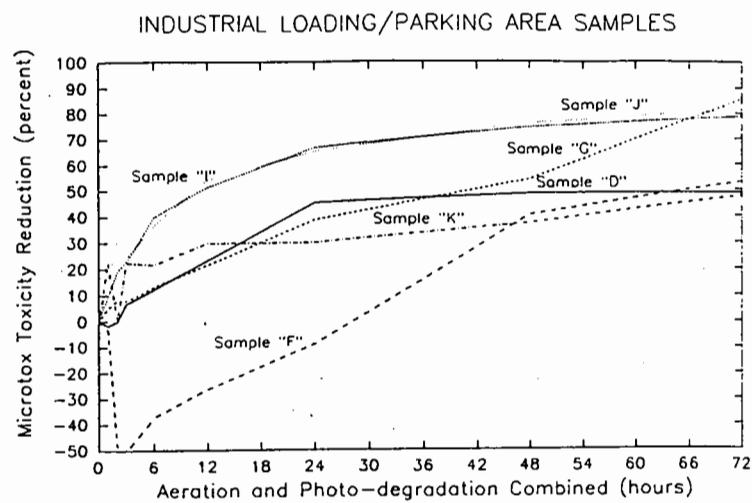
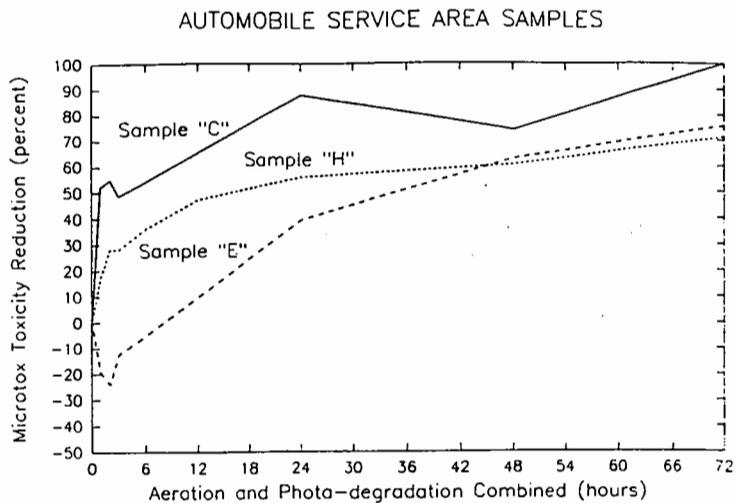
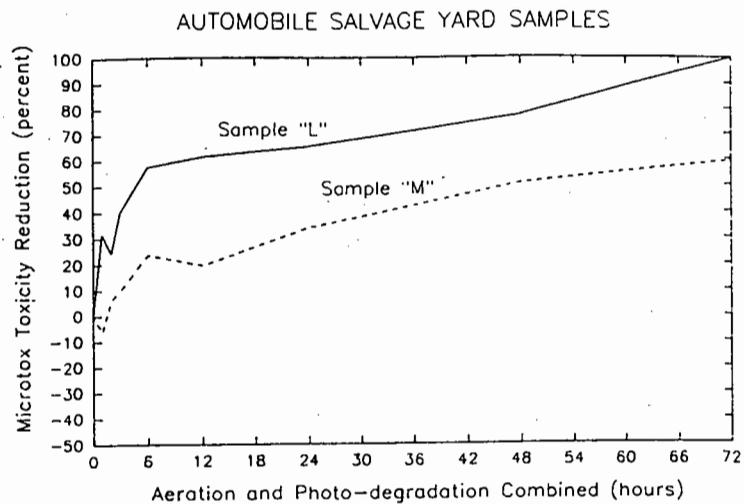


Figure 7. Aeration and photo-degradation combined treatability test toxicity trends.



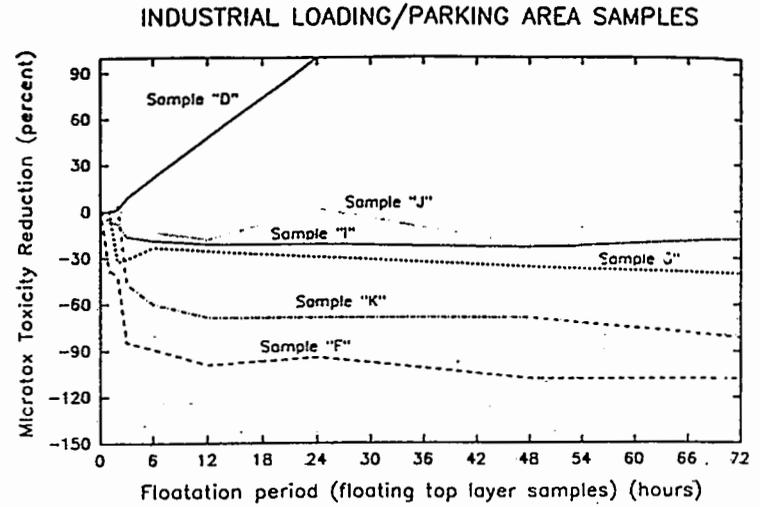
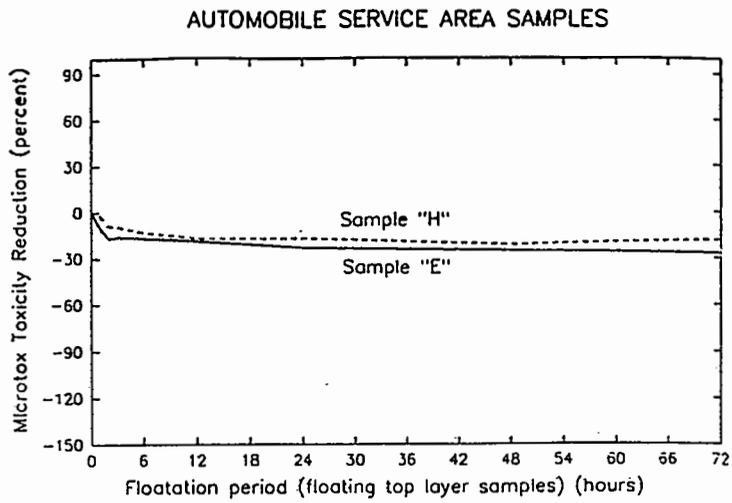
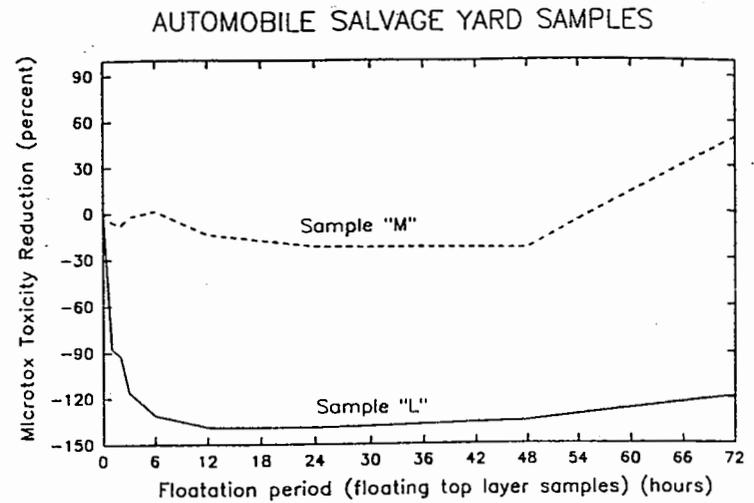


Figure 8. Flootation treatability test toxicity trends (top layer samples).



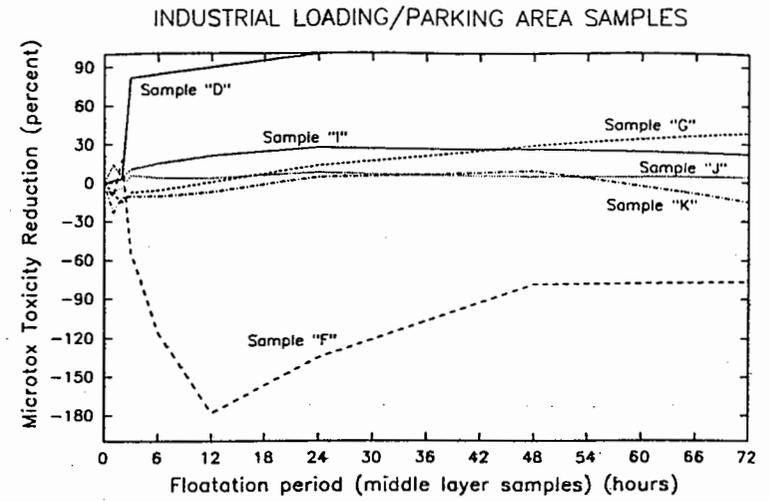
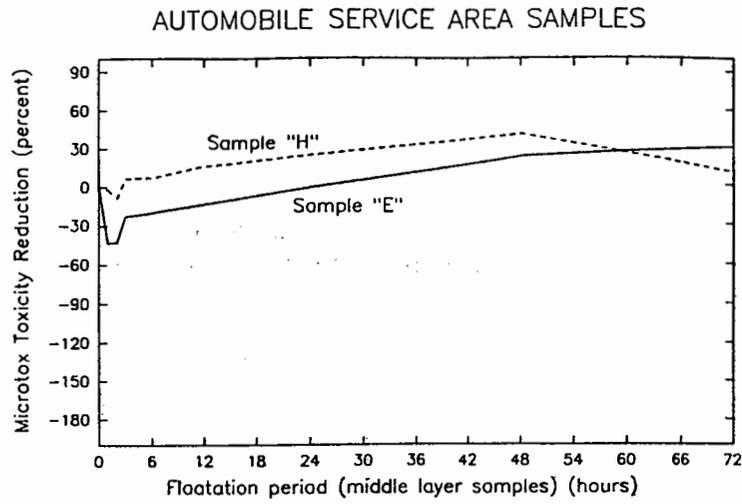
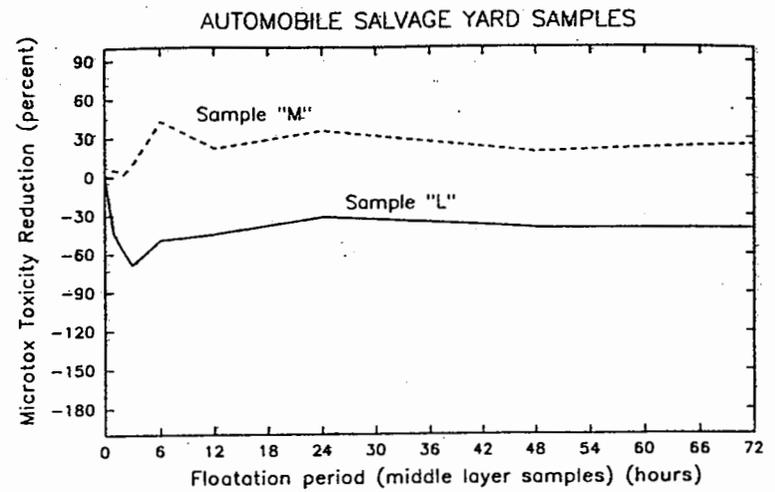


Figure 9. Flotation treatability test toxicity trends (middle layer samples).



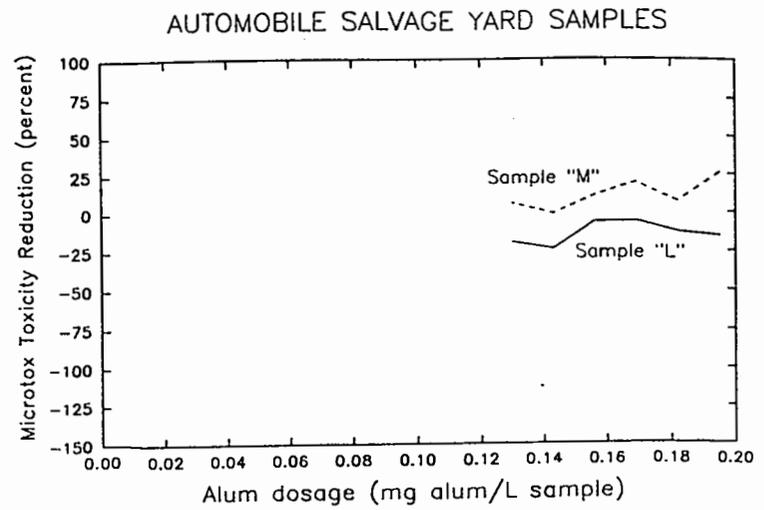
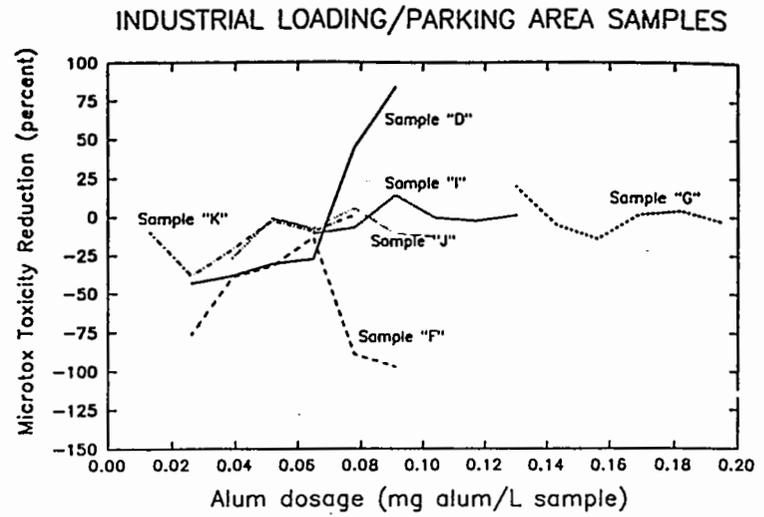
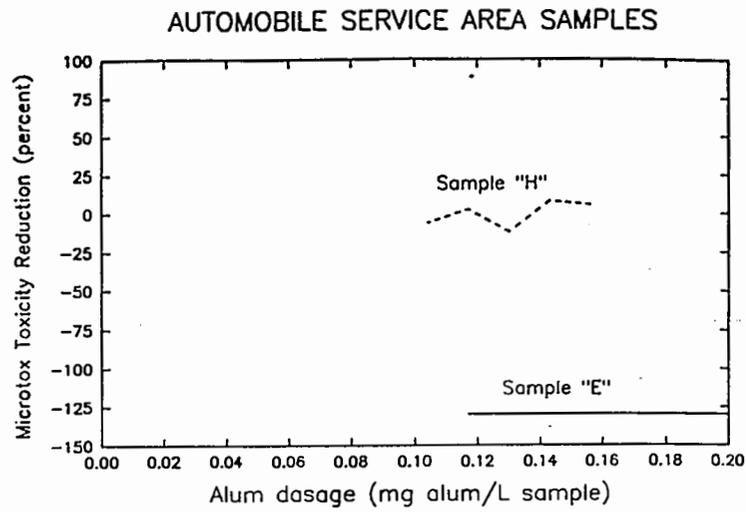


Figure 10. Alum addition treatability test toxicity trends.

REPORT ON ENHANCING EFFECTS OF LOW FREQUENCY VIBRATION IN SOIL WASHING

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ABSTRACT

The project evaluated the use of low-frequency vibrations to enhance the extraction of seven inorganic and three semivolatile organic contaminants from synthetic soils. Acid and surfactant extraction solutions were used. The contaminated soil and extractant solutions were stirred and vibrated at different frequencies and amplitudes. Vibrations increased the removal of inorganic contaminants, which originated in a compound that has a high degree of insolubility in water. The results of analytical tests for the removal of semivolatile organic contaminants were inconclusive.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

Under a U.S. EPA contract, Foster Wheeler Enviresponse, Inc. is evaluating several technologies for cleaning soil contaminated with inorganic and organic hazardous waste. One such evaluation washes contaminated soil in appropriate extractants using mechanical mixing with and without vibration. Low-frequency mechanical vibrations enhance chemical processes involving heat and mass transfer. The experiments attempted to clean materials contaminated with inorganic or semivolatile organic substances [1,2].

A literature search was conducted; a series of preliminary tests were then performed with and without low-frequency vibrations. Results in both inorganic [arsenic, cadmium, chromium, copper, nickel, lead, and zinc] and semivolatile organic [pentachlorophenol, anthracene, and bis(2-ethylhexyl)phthalate] contaminants were examined.

The test setup and procedure, the test matrix, and the results will be described; conclusions and recommendations for future work will also be presented.

## MATERIALS AND METHODS

### Literature Search

The literature search used two databases -- NERAC™ and DIALOG™. The initial goal was to find any research data available on soil washing assisted by low-frequency vibration. Search of the two databases revealed only the Harbauer method, for which only general information was available. No quantitative data on this process are readily available.

The search in DIALOG™ was then broadened to include any information on mass transfer enhancement by low-frequency mechanical vibrations. Papers in this category discussed extraction of vegetable oils, metal recovery from ores, and particle separation. These papers indicated that low-frequency mechanical vibrations do indeed assist mass transfer for various processes.

In most cases, the optimum vibration frequency was in the range of 25 to 60 hertz (Hz); amplitude was a few millimeters (mm). V.L. Demidov [3] reported recovery of gold and silver from ores using low-frequency vibration mixing.

### Vibration-Assisted Soil Cleaning Tests

The test equipment employed a mechanical shaker, a function generator, and a power amplifier. (See Figure 1.) The function generator/amplifier system provides vibratory response to the shaker table over a range of frequencies and amplitudes for different wave forms. Tests were conducted at frequencies ranging from 30 to 60 Hz and at double amplitudes from 1/32 to 1/8 inches (in) [0.8 to 3.2 mm].

Soil and extractant were put in a stainless steel beaker, which was fastened to the shaker table with a screw. An inverted plastic funnel was press-fit into the beaker opening to prevent splashing. A mechanical mixer was inserted through the funnel opening. This apparatus was used to duplicate the base case soil cleaning [1].

In the beaker, three perforated, partial, annular plates (See Figure 2.) facilitated transmission of vibratory energy to the soil-extractant mixture, while maintaining a near-normal circulation pattern. The three plates were spaced vertically to remain immersed in the solution during all tests.

In each test, the beaker was subjected to appropriate mixing and vibratory action for 30 minutes. At the end of each test, the extracting solution was decanted through a filter, followed by three 50-milliliter (ml) washings. The filtrate was analyzed for the presence of inorganic (or semivolatile organic) contaminants. For the inorganic runs, each test was interrupted every 5 minutes to adjust the pH to 1.0, by adding 6-molar nitric acid (6M HNO<sub>3</sub>) solution (a total of 20 ml added during each test).

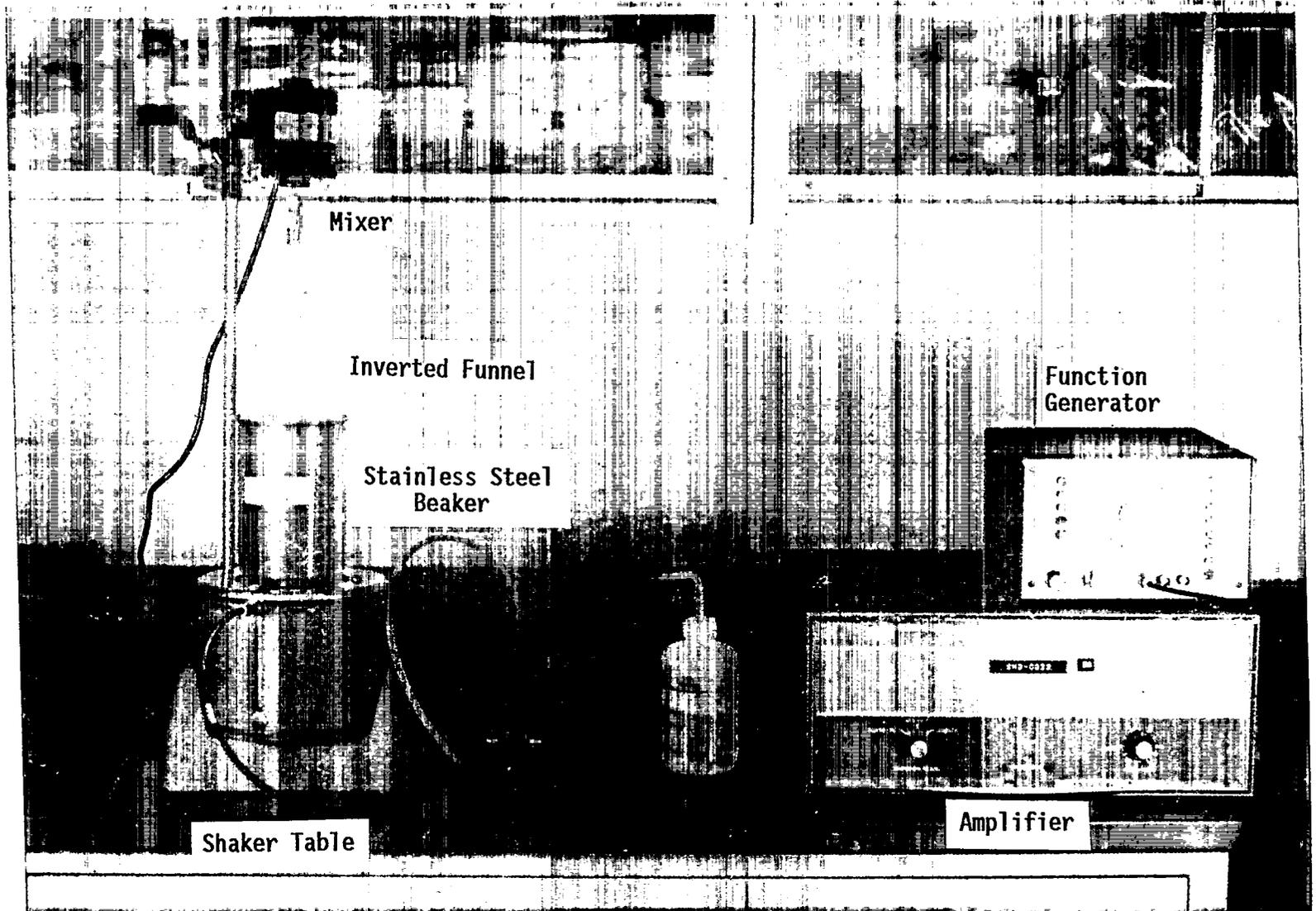


Figure 1. Vibration-assisted soil washing setup.

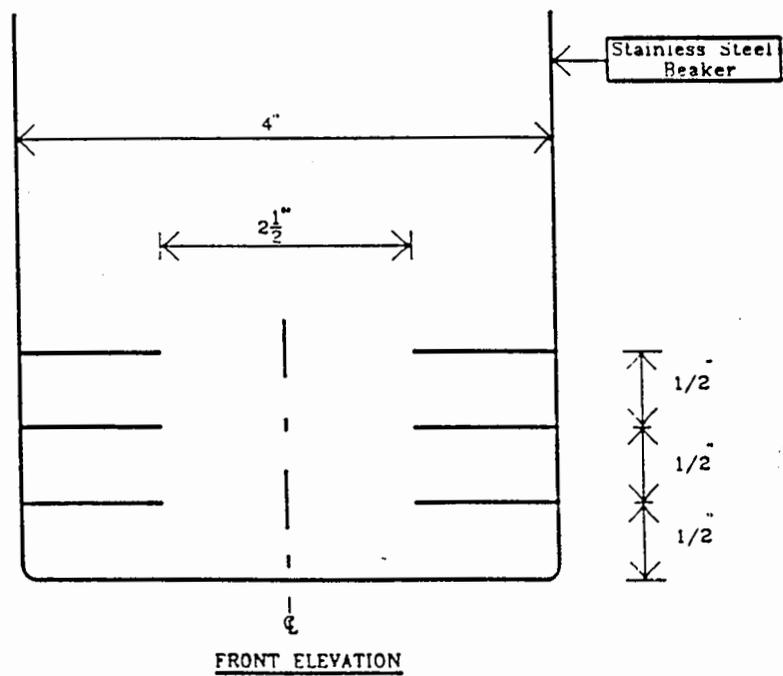
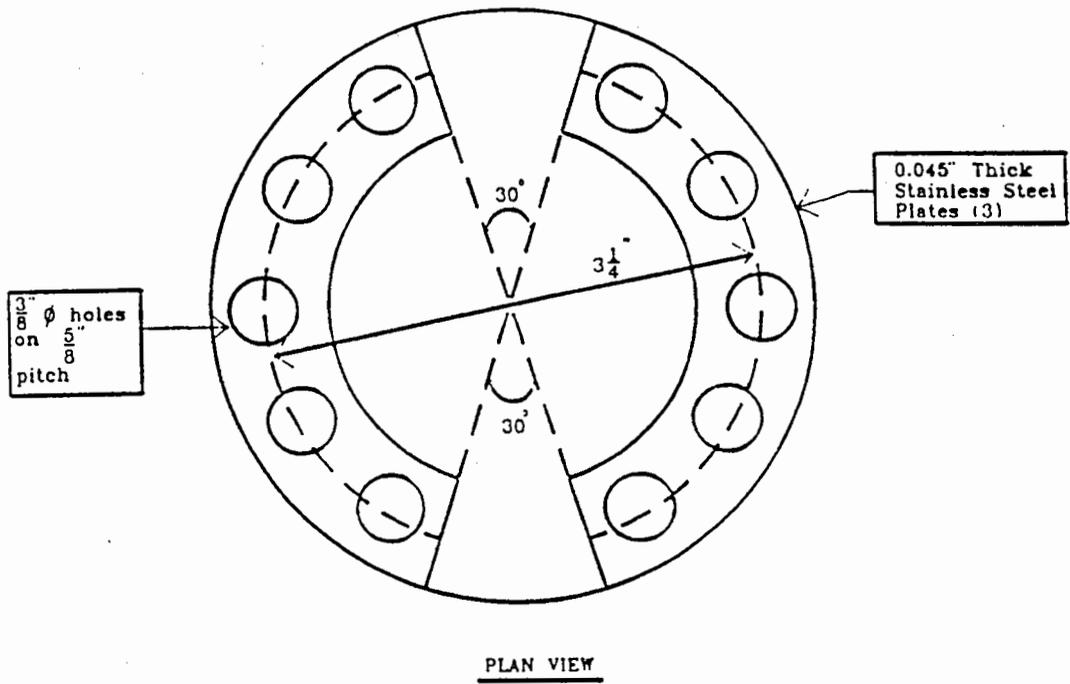


Figure 2. Vibrating beaker configuration.

Two separate sets of tests were performed: one analyzing the removal of inorganics; the other, semivolatile organics. The test conditions were chosen from the results of mixing tests conducted earlier [1,2].

For the removal of inorganics, a test from a previous study was chosen as the base case [1, Test 35]. This test was based on the following parameters:

Soil	250 to 2000 micron fraction of SARM* III
Reagent	Nitric acid (HNO <sub>3</sub> )
pH	Initial 1.0, final 1.3
Time	30 minutes
Temperature	75°F
Liquid/soil	15

This case was selected because the removal efficiencies for the contaminant metals [arsenic, cadmium, chromium, copper, nickel, lead, and zinc], using mixing, ranged from 14.5% for lead to 76.0% for cadmium -- thus leaving some room for improvement. The starting pH of 1.0 was desirable since this level was found to be most effective [1]. The 30-minute time was considered reasonable. The 74°F to 76°F temperature (ambient) eliminated the need for any heating. A total of seven tests were performed using freshly wet-sieved SARM III. All seven tests were performed in triplicate so that their precision could be assessed. The following conditions were maintained during all tests for the removal of inorganic contaminants:

Soil	250 to 2000 micron fraction of SARM III (20 gm)
Reagent	0.1M HNO <sub>3</sub> (300 gm)
Initial pH	1.0
Time	30 minutes
Temperature	Ambient
Liquid/Soil	15

\* Synthetic Analytical Reference Matrix

The first test (in triplicate) was a control case. No mechanical vibrations to the beaker were imparted; stirrer mixing was operated at 500 rpm. The remainder of the test matrix repeated the first test with vibrations at respective frequencies of 30, 45, and 60 Hz. Each frequency was tested at double amplitudes of 1/32 and 1/16 in.

The tests for removal of semivolatile organics were performed in a similar manner. Eight tests (each in triplicate) used freshly wet-sieved SARM I. Test parameters were maintained as follows:

Soil	63 to 250 micron fraction of SARM I (20 gm)
Reagent	0.75% Achowet Surfactant (100 gm)
Time	30 minutes
Temperature	Ambient
Liquid/Soil	5

The first test was the control test. No vibrations were employed; stirrer mixing was operated at 500 rpm. The remaining seven tests added vibrations at three different frequencies (30, 45, and 60 Hz) and varying amplitudes of 1/32, 1/16, and 1/8 in.

Technology Applications, Inc. of Cincinnati conducted all soil and filtrate analyses for the presence of inorganic and semivolatile organic contaminants. The inorganics analyses measured arsenic, cadmium, chromium, copper, nickel, lead, and zinc. The semivolatile organics analyses quantified the presence of pentachlorophenol, anthracene, and bis(2-ethylhexyl)phthalate.

The SARM III (250-2000  $\mu\text{m}$ ) and SARM I (63-250  $\mu\text{m}$ ) feed samples were analyzed in triplicate to provide the base contaminant levels. All filtrates from the seven triplicate inorganic tests and the eight triplicate semivolatile organic tests were analyzed to determine contaminant removal efficiencies.

## RESULTS AND DISCUSSION

### Inorganics

#### Feed Soil Analysis

Table 1 provides the analysis of the SARM III feed, performed in triplicate. It also shows the arithmetic means (x).

TABLE 1. ANALYSIS OF SARM III (250-2000  $\mu\text{m}$  fraction) FEED

Contaminants	Replicates			x
	1	2	3	
Arsenic	183	165	178	175
Cadium	432	402	414	416
Chromium	86.5	102	137	109
Copper	1008	1360	1771	1380
Nickel	128	148	178	151
Lead	4725	4416	5953	5031
Zinc	3361	4148	5927	4479

Replicates: Concentration of contaminants in soil (mg/kg) from identical experiments.

x: Arithmetic mean of three values (mg/kg)

#### Filtrate Analysis

Table 2 summarizes the results of the seven triplicate tests for removal of inorganic contaminants. It also shows the arithmetic means (x).

#### Material Balance

Table 3 summarizes the material balance data for six tests on removal of inorganics. It gives "Percent Extracted" and "Percent Remaining on Soil"

TABLE 2. SUMMARY OF EXTRACTION RESULTS -- INORGANIC CONTAMINANTS

Test description	Contaminant	Test replicates			x
		B1	B2	B3	
Stirring, no vibration		B1	B2	B3	
	Arsenic	57.8	60.1	62.3	60.1
	Cadmium	72.8	75.2	85.8	77.9
	Chromium	84.5	84.9	83.3	84.2
	Copper	82.6	89.1	75.3	82.3
	Nickel	107.7	92.2	78.6	92.8
	Lead	60.1	61.0	59.0	60.0
	Zinc	71.6	76.5	78.2	75.4
30 Hz, 1/16 in, da (low-frequency vibration)		2A	2B	2C	
	Arsenic	77.8	62.4	62.6	67.6
	Cadmium	123.8	99.9	86.2	103.3
	Chromium	96.7	89.3	83.8	89.9
	Copper	85.2	78.9	77.3	80.5
	Nickel	105.2	90.5	83.1	92.9
	Lead	107.9	74.2	80.7	87.6
	Zinc	107.2	87.1	82.6	92.3
30 Hz, 1/32 in, da (low-frequency vibration)		3A	3B	3C	
	Arsenic	59.0	60.7	62.0	60.6
	Cadmium	85.9	83.1	84.1	84.4
	Chromium	76.0	70.4	80.0	75.5
	Copper	67.9	64.4	72.2	68.2
	Nickel	73.9	70.2	77.7	73.9
	Lead	61.9	61.6	65.8	63.1
	Zinc	73.1	66.0	74.6	71.2
45 Hz, 1/16 in, da (low-frequency vibration)		4A	4B	4C	
	Arsenic	70.8	64.9	64.3	66.7
	Cadmium	87.1	87.4	86.0	86.8
	Chromium	92.7	77.0	77.3	82.3
	Copper	84.9	69.3	71.7	75.3
	Nickel	89.8	78.4	77.3	81.8
	Lead	94.0	87.4	87.8	89.7
	Zinc	90.2	75.4	77.6	81.1

(continued)

TABLE 2. Continued

Test description	Contaminant	Test replicates			x
45 Hz, 1/32 in, da (low-frequency vibration)		5A	5B	5C	
	Arsenic	66.0	62.9	61.5	63.5
	Cadmium	86.7	92.1	82.3	88.7
	Chromium	80.0	76.4	77.3	77.9
	Copper	73.8	72.7	73.1	73.2
	Nickel	80.0	79.0	77.0	78.7
	Lead	81.1	76.1	74.5	77.2
Zinc	79.0	78.1	75.2	77.4	
60 Hz, 1/16 in, da (low-frequency vibration)		6A	6B	6C	
	Arsenic	65.5	63.8	66.3	65.2
	Cadmium	86.1	86.2	85.6	86.0
	Chromium	82.8	82.3	82.3	82.5
	Copper	75.8	77.6	73.6	75.7
	Nickel	81.0	80.0	77.7	79.6
	Lead	94.9	85.9	93.7	91.5
Zinc	78.9	75.5	79.9	78.1	
60 Hz, 1/32 in, da (low-frequency vibration)		7A	7B	7C	
	Arsenic	63.2	62.6	60.3	62.0
	Cadmium	86.4	89.6	82.3	86.1
	Chromium	80.5	76.4	80.0	79.0
	Copper	75.0	67.8	71.6	71.5
	Nickel	81.4	74.7	77.7	77.9
	Lead	83.0	78.1	91.7	84.3
Zinc	82.0	71.7	77.6	77.1	

Replicates: Percentages extracted from three identical experiments  
x: Arithmetic mean of three values, %  
da: Double amplitude

TABLE 3. MATERIAL BALANCE DATA -- INORGANICS

Test	Contaminant	Percent extracted	Percent remaining on soil	Percent recovered*
B1	Arsenic	57.8	46.6	104.4
	Cadmium	72.8	13.5	86.3
	Chromium	84.5	12.3	96.8
	Copper	82.6	8.7	91.3
	Nickel	107.7	10.7	118.4
	Lead	60.1	40.9	101.0
	Zinc	71.6	7.7	79.3
B3	Arsenic	62.3	56.9	119.2
	Cadmium	85.8	22.3	108.1
	Chromium	83.3	11.4	94.7
	Copper	75.3	14.1	89.4
	Nickel	78.6	12.7	91.3
	Lead	59.0	56.5	115.5
	Zinc	78.2	10.0	88.2
2A	Arsenic	77.8	43.1	120.9
	Cadmium	123.8	10.6	123.4
	Chromium	96.7	9.5	106.2
	Copper	85.2	7.1	92.3
	Nickel	105.2	9.3	114.5
	Lead	107.9	21.8	129.7
	Zinc	107.2	4.6	111.8
2C	Arsenic	62.6	42.3	104.9
	Cadmium	86.2	8.3	94.5
	Chromium	83.8	15.5	99.3
	Copper	77.3	8.0	85.3
	Nickel	83.1	8.7	41.8
	Lead	80.7	34.6	115.3
	Zinc	82.6	6.2	88.8
7A	Arsenic	63.2	55.4	118.6
	Cadmium	86.4	18.1	104.5
	Chromium	80.5	12.3	92.8
	Copper	75.0	8.5	83.5
	Nickel	81.4	10.0	91.4
	Lead	83.0	13.8	96.8
	Zinc	82.0	5.6	87.6

(continued)

TABLE 3. Continued

Test	Contaminant	Percent extracted	Percent remaining on soil	Percent recovered*
7B	Arsenic	62.6	40.0	102.6
	Cadmium	89.6	13.7	103.3
	Chromium	76.4	16.4	92.8
	Copper	67.8	26.1	93.9
	Nickel	74.7	10.7	85.4
	Lead	78.1	15.1	93.2
	Zinc	71.7	5.4	77.1

\* Amount of contaminant in feed soil

values for each inorganic contaminant. The sum of these two percentages should ideally be 100; the calculated values are shown as "Percent Recovered." As seen in Table 3, most "Percent Recovered" values fall between 80 and 120, indicating good material balance.

#### Extraction Efficiency

Table 4 summarizes the average percent removal efficiencies for the seven inorganics tests. Symbols indicate improvement (y) or lack of improvement (n), relative to the no-vibration control case.

Table 4 also lists the seven inorganic compounds in SARM III and their solubility in cold water. Table 5 shows the percent increase in extraction efficiency over the no-vibration control case.

TABLE 4. AVERAGE PERCENTAGE EXTRACTION RESULTS -- INORGANIC CONTAMINANTS

Description Double amplitude (in) Test	Stirring, no vibration B1,2,3	30 Hz		45 Hz		60 Hz		Metal source		
		1/16 2A,B,C	1/32 3A,B,C	1/16 4A,B,C	1/32 5A,B,C	1/16 6A,B,C	1/32 7A,B,C	Solubility*		
<u>Metals</u>										
Arsenic (As)	60.1	67.6 y	60.6 y	66.7 y	63.5 y	65.2 y	62.0 y	1.2(0')	As <sub>2</sub> O <sub>3</sub>	
Cadmium (Cd)	77.9	103.3 y	84.4 y	86.8 y	88.7 y	86.0 y	86.1 y	114(0')	3CdSO <sub>4</sub> ·8H <sub>2</sub> O**	
Chromium (Cr)	84.2	89.9 y	75.5 n	82.3 n	77.9 n	82.5 n	79.0 n	s	Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O**	
Copper (Cu)	82.3	80.5 n	68.2 n	75.3 n	73.2 n	75.7 n	71.5 n	24(0')	CuSO <sub>4</sub> ·5H <sub>2</sub> O**	
Nickel (Ni)	92.8	92.9 y	73.9 n	81.8 n	78.7 n	79.6 n	77.9 n	243(0')	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O**	
Lead (Pb)	60.0	87.6 y	63.1 y	89.7 y	77.2 y	91.5 y	84.3 y	0.004(18')	PbSO <sub>4</sub> ·PbO	
Zinc (Zn)	75.4	92.3 y	71.2 n	81.1 y	77.4 y	78.1 y	77.1 y	0.004(18')	ZnO	

\* Solubility in 100 parts cold water [degrees in Centigrade; s = soluble]

\*\* Water-soluble compounds

y/n Indicates improvement (y) or lack of improvement (n) relative to "no-vibration" mode

TABLE 5. PERCENT INCREASE IN INORGANICS EXTRACTION EFFICIENCY OVER CONTROL CASE

Test	Stirring, no vibration	30 Hz		45 Hz		60 Hz	
		1/16"	1/32"	1/16"	1/32"	1/16"	1/32"
Metal	B1, 2, 3*	2A,B,C	3A,B,C	4A,B,C	5A,B,C	6A,B,C	7A,B,C
Arsenic	-	12	1	11	6	8	3
Cadmium	-	32	8	11	14	10	11
Chromium	-	7	-10	-2	-7	-2	-6
Copper	-	-2	-17	-9	-11	-8	-13
Nickel	-	0	-20	-12	-15	-14	-16
Lead	-	46	5	50	29	53	41
Zinc	-	22	-6	8	3	4	2

\* Control Case

The following observations are based on the results presented in Tables 4 and 5:

- o Vibration improved the extraction of arsenic, lead, cadmium, and zinc.
- o The effect of vibration was more enhanced at 1/16 in (double amplitude) than that at 1/32 in.
- o In general, the enhancement due to vibration improved at lower frequencies; 30 Hz at 1/16 in (double amplitude) resulted in maximum enhancement.
- o Lead showed the maximum enhancement due to vibration.
- o Test precision is well within the guideline value of 30% relative standard deviation for all tests.

## Semivolatile Organics

### Feed Soil Analysis

Table 6 provides the analysis of SARM I (63-250  $\mu\text{m}$ ) feed performed in triplicate. It also shows the arithmetic means (x).

TABLE 6. ANALYSIS OF SARM I (63-250  $\mu\text{m}$  fraction) FEED

Contaminant	Replicates			x
	1	2	3	
Pentachlorophenol	300	305	310	305
Anthracene	7895	8230	6860	7662
Bis(2-ethylhexyl)phthalate	801	775	850	809

Replicates: Concentration of contaminants in soil (mg/kg) from identical experiments

x: Arithmetic mean of three values (mg/kg)

### Filtrate Analysis

Table 7 presents the results of the eight triplicate tests for the removal of semivolatile organics.

### Material Balance

Very poor material balance data were obtained for all semivolatile organic tests. The lack of material balance may be caused by the analytical techniques employed. This makes suspect any evaluation of the degree of extraction enhancement due to vibration.

TABLE 7. AVERAGE PERCENTAGE EXTRACTION RESULTS -- ORGANIC CONTAMINANTS

Description Double amplitude (in) Test	Stirring, no vibration 0 1A,B,C	30 Hz			45 Hz		60 Hz	
		1/8 2A,B,C	1/16 3A,B,C	1/32 4A,B,C	1/16 5A,B,C	1/32 6A,B,C	1/16 7A,B,C	1/32 8A,B,C
Compound								
Pentachlorophenol	28.2	13.0	21.6	27.1	37.5	33.5	17.9	26.2
% Increase over "Control"		-54 n	-23 n	-4 n	+33 y	+19 y	-37 n	-7 n
Anthracene	0.15	0.043	0.10	0.35	0.29	0.34	0.29	0.34
Bis(2-ethylhexyl)phthalate	2.01	1.11	0.29	10.8	12.9	5.0	4.4	2.63
% Increase over "Control"		-45 n	-86 n	+437 y	+541 y	+149 y	+119 y	+29 y

y/n Indicates improvement (y) or lack of improvement (n) relative to "no-vibration" mode

## Extraction Efficiency

Table 7 summarizes the average percent removal efficiencies for the eight semivolatile organic tests. It shows the percent increase in extraction efficiency over the no-vibration control case for pentachlorophenol and bis(2-ethylhexyl)phthalate. Such values for anthracene are eliminated due to very small removal efficiencies.

## CONCLUSIONS

### Inorganics

1. The limited tests of vibration-assisted soil washing show an improvement in removal efficiency for basic lead sulfate ( $\text{PbSO}_4 \cdot \text{PbO}$ ),  $\text{As}_2\text{O}_3$  and  $\text{ZnO}$  which is relatively insoluble in water. Water-soluble compounds were extracted, to a large extent, by the mixing action alone; there was little enhancement with vibration, with the exception of hydrated cadmium sulfate ( $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ) -- which is water-soluble -- showed extraction enhancement due to vibration.
2. In general, vibration enhancement for inorganics improved at the larger of the two amplitudes tested (1/16 in and 1/32 in), and at lower frequencies (30 Hz).
3. The triplicate test data analysis shows good precision for the inorganics. Good material balances were also obtained.

### Semivolatile Organics

1. The semivolatile organics tests showed very little extraction of anthracene with and without vibration. There was a complete lack of material balance for all three semivolatile organics. The analyses of the triplicate test results showed inadequate precision for most tests. Therefore, no meaningful conclusions can be drawn from the results obtained for the extraction of semivolatile organic contaminants.

## RECOMMENDATIONS

Further work should be performed to establish definitive quantitative trends. It should include the following:

### General

- o Further tests on alternate extractants are necessary to draw sound conclusions on the enhancement of soil washing by low-frequency vibration.
- o Frequency and amplitude effects should be explored; a large range of amplitudes should be investigated. This would necessitate the use of improved vibration equipment that would allow testing at a wider range of frequencies and amplitudes (such as a vibrating screw device).
- o Tests with different time durations should be conducted to evaluate optimum elapsed times.
- o Further testing should include evaluation of vibration enhancement for differing sizes of soil fractions. Varying liquid-to-solid ratios should also be investigated.
- o The use of alternative extractants and the effect of heating in the tests should be considered.

### Inorganics

- o Further testing should incorporate better pH control so its influence can be excluded from the results. This will facilitate more meaningful comparisons and performance evaluations. It could involve two sets of experiments. In one set, short-time (10-min) tests without any pH adjustments can determine relative performance. In another, longer-term (30- to 60-min) tests can be conducted, but with more frequent pH adjustments so that all tests have close pH control.

## Semivolatile Organics

- o Additional surfactants should be tested.

### ACKNOWLEDGEMENTS

This study was sponsored by the Releases Control Branch of the EPA Risk Reduction Engineering Laboratory, under Contract No. 68-C9-0033 to Foster Wheeler Enviresponse, Inc. and Foster Wheeler Development Corporation. This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policy and approved for presentation and publication.

The authors gratefully acknowledge the assistance provided by P. Steiner, K. Ahluwalia, and E. Gonzalez of Foster Wheeler Development Corp. in conducting the program. Additional thanks are due to M. Krawchuk who assembled the test apparatus. Technology Applications, Inc. provided all analytical services.

The support of the Foster Wheeler Enviresponse, Inc. staff is deeply appreciated, especially the technical input of R. Gaire and the editing by Marilyn Avery. RCB technical reviewers also assisted in editing this work.

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VACUUM-ASSISTED STEAM STRIPPING TO REMOVE POLLUTANTS FROM CONTAMINATED  
SOIL A LABORATORY STUDY

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ABSTRACT

Previous work on this project was involved with a laboratory study of the viability of steam stripping a variety of organic chemicals from a number of soil types with water permeabilities between  $10^{-3}$  and  $10^{-6}$  cm/s. The range of permeabilities was achieved by mixing appropriate amounts of sand and silt. In this study the effects of a clay fraction and organic fraction in the soil are investigated. Results are shown for a predominately sand/silt soil but also with:

- varying amounts of clay (kaolinite and bentonite were used)
- varying amounts of organic material (a commercial top soil was used)

The effect of a "delay time" (i.e., interruption time) in decontamination procedure is studied. The initial rate of chemical removal immediately upon resumption of treatment is compared with the rate immediately before interruption.

A new analytical model for vacuum-assisted steam stripping using a circular symmetry model is developed. Some relevant experiments were run to obtain data which allow the model to be used more confidently estimating decontamination times for a given spill scenario.

INTRODUCTION AND OVERVIEW

In the case of contaminated soils at Superfund (and other) sites, it is important that the chemicals present be prevented from reaching the

groundwater. In many locations fortunately a partially saturated or vadose zone exists and acts as a temporary containment retarding the downward movement of the pollutant. The possible remediation options are:

- Excavation and off-site disposal.
- Excavation and on-site treatment.
- Insitu treatment (via a number of possible methods, e.g., biological, physical or chemical).

A number of these techniques (and others) have been reviewed in other articles (1,2). These in-situ techniques have been discussed by the authors (3). A review of decontamination techniques is given in reference 4.

The present study falls into the in-situ treatment category wherein the authors propose to have pipes inject steam into the soil beneath the contaminated zone. Steam stripping of the chemical occurs and aided by a vacuum at the ground surface, transports the contaminants to a collection point where they can be properly treated. A unique aspect of the study is the development of a geosynthetic cap assembly consisting of a high transmissivity geotextile and a flexible membrane liner (geomembrane). The vacuum is applied to the underside of this liner and the contaminated gas and/or liquid moves beneath the liner in the geotextile to the outlet ports. A schematic diagram of a proposed system is given in Figure 1.

There have been a few steam stripping soil decontamination studies reported in the literature (5,6,7,8). These works were field-oriented, sites-of-opportunity projects with no attempt to look at the general problem of the feasibility of steam stripping a wide variety of chemicals from a wide variety of soils.

The present work continues a long term study to determine the ability of vacuum-assisted steam stripping to decontaminate general organic chemical species from a variety of soil types.

#### PREVIOUS WORK ON THIS PROJECT

The work performed previously on this project has been reported in detail elsewhere (3,9,10,11,12). Only a brief review of the results of this work will be given here. More detail can be found in the cited references. Among the tasks undertaken, in a wide variety of soils:

- Observations were made of the transient steam front movements in two dimensional flow.
- The steam permeabilities were determined in conventional one-dimensional flow.
- The efficiency of steam stripping kerosene and a number of

individual organic chemicals from soils was determined. The chemicals included dodecane, decane, octane, octanol and butanol. The analytical methods included either volume separation of the outflow material (for kerosene) or gas chromatography (GC) of extractions from the soil (for the compounds). Work was done in regard to determining the limits of confidence in the soil extraction/gas chromatography analytical procedure.

- The effect of steam pressure and temperature on the steam stripping capability was determined.
- Comparison of the efficiency of steam stripping versus the other common in-situ techniques, i.e., air stripping, vacuum extraction and heat alone.
- A steady state analytical model was developed where steam flows upward to the collection cap from pipes embedded in the soil. Use of this model allows calculation of the decontamination time for a given spill. Due to certain objections raised concerning the previous model and its use, a new model is presented here and analytical results given.
- A small scale model of the geosynthetic cap was fabricated and used to determine its feasibility as a cover assembly during steam stripping.

It was felt that the results from the above topics indicated that the vacuum-assisted steam stripping technique showed significant promise as a soil decontamination method for a wide range of soil types and chemicals.

The authors deemed that some additional work would be necessary in helping to evaluate the feasibility of using vacuum-assisted steam stripping to remove organic chemicals from soil. These items were:

- The effect of a clay fraction in the soil on the chemical removal efficiency.
- The effect of an organic fraction in the soil on the chemical removal efficiency.
- The development of a better theory with which to determine the time to decontaminate a given soil/chemical situation.
- The effect of a delay time in the decontamination processing upon the relative rate of chemical removal.

The next Section describes the results of this work.

#### PRESENT WORK

##### EFFICIENCY OF ORGANIC CHEMICAL REMOVAL VIA VACUUM-ASSISTED STEAM STRIPPING

It was decided in the interest of better use of the graduate student's time that the soil extractions and gas chromatography work would be handled by a firm specializing in this type of chemical

analytical work. Fortunately we were able to obtain the services of Technology Application, INC., who do soil chemistry work for the U.S. EPA, EMSL Analytical Support Laboratory in Cincinnati.

The matrix of chemicals and soil types which were used in vacuum-assisted steam stripping studies are shown in Table 1. We chose to work with dodecane because it is a very difficult chemical to remove due to its low vapor pressure (boiling point = 216°C). It thus presents an extreme test for the vacuum-assisted, steam stripping decontamination procedure. The benzene/ethyl benzene/toluene/xylene (BETX) was chosen for it is a commonly-used simulant for gasoline. The soil extraction procedure and gas chromatography approach were the method of analysis, as was the case in earlier work described in references 12 and 13. The only differences were that Soxhlet extraction was used here instead of mechanical agitation of the mixed extraction fluid and soil used earlier (11,12). In the Soxhlet work here, methylene chloride was used as the extraction fluid. In our earlier work, either methylene chloride (11) or ethyl ether (12) was used as the extraction fluid.

The vacuum-assisted steam stripping runs were performed with the apparatus described earlier (3) and shown in Figure 2. The sample cells were now made of brass instead of plexiglass, for the BETX was extremely corrosive to plexiglass. The steam pressure was 5 psi gauge at the input end in all cases, and full vacuum was applied at the other end. (The vacuum amounted to about 10-inches of Hg for the sand and up to 20-inches of Hg for the silt.)

The results are given in Table 1. It is seen that the level of dodecane can be reduced much lower in sand than in the 50 sand/50 silt. Of course the flow is smaller in the 50/50 soil than in the sand (about 6-times slower). It is felt that the results are quite favorable considering that dodecane has an extremely high boiling point and the steam stripping treatment times were not overly long.

The other materials involved in the other entries in Table 1 are currently being worked on and results will be presented at the Conference.

#### EFFICIENCY OF ORGANIC CHEMICAL REMOVAL VIA VACUUM EXTRACTION

Although vacuum extraction studies per se, were not part of our initial work plan, we have found them over the course of our work to be very productive experiments to ascertain the "binding ability" of organic chemicals to particular soil types. Screening experiments (using a variety of soils) can be performed much quicker with vacuum extraction than with the much more time-consuming steam stripping measurements. Of course our ultimate goal is to ascertain the feasibility of steam stripping organic chemicals from a wide range of soils.

TABLE 1. RESULTS OF VACUUM-ASSISTED STEAM STRIPPING EXPERIMENTS

Chemical	Initial Concentration (% and ppm)	Soil Type	Time of Treatment (hours)	Average Final Concentration (with Standard Deviation) (ppm)	Amount Removed (%)
Dodecane	5% 50,000 ppm	Beach Sand	2	421 ± 53 (n = 5)	99.2
Dodecane	5% 50,000 ppm	50 Sand 50 Silt	8	3826 ± 2070 (n = 5)	92.4
Dodecane	5% 50,000 ppm	45 Sand 45 Silt 10 Kaolinite	8		
Dodecane	5% 50,000 ppm	48 Sand 48 Silt 4 Bentonite	8		
Dodecane	5% 50,000 ppm	45 Sand 45 Silt 10 organic			
• Benzene • Ethyl- Benzene • Toluene • Xylene (BETX)	2% each 20,000 ppm each	Beach Sand	2		
BETX	2% each 20,000 ppm each	50 Sand 50 Silt	8		
BETX	2% each 20,000 ppm each	45 Sand 45 Silt 10 Kaolinite	8		
BETX	2% each 20,000 ppm each	48 Sand 48 Silt 4 Bentonite	8		
BETX	2% each 20,000 ppm each	45 Sand 45 Silt 10 Organic	8		

Figure 3 shows a schematic diagram of the soil cell in the furnace. The cell size is the same as for the steam stripping experiments. The main thrust in these experiments was to ascertain how the rate of kerosene removal was affected by the addition of a clay and an organic fraction to the 50 sand/50 silt type soil. The experimental procedure is the same as discussed in reference 13. Figure 4 shows the results of a 45 sand/45 silt/10 kaolinite soil. (The results of the 50/50 soil are shown for reference purposes.) It is observed that the rate of kerosene removal has been perceptively slowed (from the 50 sand/50 silt soil) by the addition of the kaolinite fraction. Figure 5 indicates results for the addition of 10% bentonite and 10% organic (i.e., top soil) with the sand/silt mixture. It is surprising that the bentonite-doped-soil does not have a slower removal rate than the kaolinite-doped-soil.

#### EFFECTS OF A DELAY TIME IN DECONTAMINATION PROCEDURE

There have been indications in the field that if vacuum extraction is performed for a given period, and then stopped, the initial rate of contaminant removal upon resumption of treatment is much larger than the final rate before stopping treatment. We have attempted to model this "delay effect" in the laboratory in order to gain insight into the problem. The emphasis will be upon the effect of soil type on the "delay effect". The procedure is the same as in the vacuum extraction studies described in the previous section with the exception that the treatment is stopped at about 50% kerosene removal. Then the sample is sealed tightly and stored for a given "delay time" before the resumption of the vacuum treatment.

Some results for the 50/50 soil is shown in Figure 6.

Results for 45/45/10 kaolinite clay are shown in Figure 7.

## ANALYTICAL MODEL FOR VACUUM-ASSISTED STEAM STRIPPING

In a previous work (3) a theoretical model was developed, with the ultimate goal of determining the decontamination time for a given chemical spill. The model used a point steam source buried beneath the surface and collection over a wide area on the surface. The model could be called a point steam source buried in a semi-infinite half space. Unfortunately, much too high steam pressures (unrealistic values) were used in the calculation. In the present work a model based on circular symmetry will be used. This symmetry may be closer to that actually used in the field. The model is shown in Figure 8. Electrical field mapping experiments (13) have shown that the pressure contours and flow lines will essentially conform to circular symmetry whenever eight or more sources (sinks) are employed symmetrically around the center sink (source). Both the dc electric field and the steady state pressure profiles are governed by Laplace's Equation.

In steady state, with constant temperature<sup>1</sup>, the steam pressure, P, will be governed by Laplace's Equation, which in the cylindrically-symmetric case can be written:

$$\nabla^2 P = \frac{1}{r} \frac{d}{dr} \left( r \frac{dP}{dr} \right) = 0 \quad (1)$$

where

r is the radial position as shown in Figure 9.

With the boundary conditions:

P = 0 at r = r<sub>o</sub> (inner pipe radius)

P = P<sub>d</sub> at r = r<sub>d</sub> (the outer pipe's distances from the center),

the solution of Equation (1) is:

$$P = \frac{P_d}{\ln \left( \frac{r_d}{r_o} \right)} \ln \left( \frac{r}{r_o} \right) \quad (2)$$

We use Darcy's law in the following vector form

---

<sup>1</sup>We have performed experiments on a small cylindrically-symmetric steam flow device of dimension 10-inch diameter and 1 foot high, with steam introduced in the center and sand as the soil. The temperature of the entire mass of soil was 100°C, once steady state was achieved. The same constancy of temperature was also achieved in earlier two-dimensional work. (3,9)

$$\vec{V} = -k \vec{\nabla}P \quad (3)$$

where

→  
 $V$  is the steam vector velocity  
 $k$  is the permeability of the steam, and  
 →  
 $\nabla P$  is the pressure gradient vector

In the case of cylindrical symmetry, Equation (3) reduces to

$$V = -k \frac{dP}{dr} \quad (4)$$

where  $V$  is the radial velocity. Using equation (2) in Equation (4) we arrive at

$$V = -k \frac{P_d}{\ln \left( \frac{r_d}{r_o} \right)} \frac{1}{r} \quad (5)$$

The volume flow rate,  $Q$ , through a lateral surface of length,  $l$ , is (see Figure 9)

$$Q = VA \quad (6)$$

( $A$  is the lateral surface area,  $2\pi rl$ )

$$Q = \left[ -k \frac{P_d}{\ln \left( \frac{r_d}{r_o} \right)} \frac{1}{r} \right] [2\pi rl]$$

$$Q = -k \frac{P_d}{\ln \left( \frac{r_d}{r_o} \right)} 2\pi l \quad (7)$$

In steady state,  $Q$  must be a constant as a function of  $r$ , as is reflected in Equation (7), i.e., the volume flow rate does not depend on  $r$ .

The values of steam permeability,  $k$ , can be obtained most easily in one dimensional flow experiments such as those described earlier (3,10,11,12). Using the value of  $k$  determined earlier in our experiments (actually  $k P_d = k\Delta P$ , is more readily accessible), the following results for velocity flows, using Equation 4, are given in Table 2. Here we can

TABLE 2. STEAM VELOCITIES AS A FUNCTION OF VARIOUS PARAMETERS

$\Delta P = 10 \text{ psi}$

$r_d/r_o$	5m/0.2m = 25	3m/0.2m = 15	3m/0.4m = 7.5	5m/0.5 = 10
V (m/s) r (m)	$3.9 \times 10^{-6} \text{ 1/r (m)}$	$4.6 \times 10^{-6} \text{ 1/r (m)}$	$6.26 \times 10^{-6} \text{ 1/r (m)}$	$5.4 \times 10^{-6} \text{ 1/r (m)}$
0.5	$7.8 \times 10^{-6}$	$9.2 \times 10^{-6}$	$1.25 \times 10^{-5}$	$1.1 \times 10^{-5}$
1.0	$3.9 \times 10^{-6}$	$4.6 \times 10^{-6}$	$6.25 \times 10^{-6}$	$5.4 \times 10^{-6}$
2.0	$1.95 \times 10^{-6}$	$2.3 \times 10^{-6}$	$3.1 \times 10^{-6}$	$2.7 \times 10^{-6}$
3.0	$1.3 \times 10^{-6}$	$1.5 \times 10^{-6}$	$2.1 \times 10^{-6}$	$1.8 \times 10^{-6}$
4.0	$0.98 \times 10^{-6}$			$1.35 \times 10^{-6}$
5.0	$0.8 \times 10^{-6}$			$1.1 \times 10^{-6}$

$\Delta P = 20 \text{ psi}$

$r_d/r_o$	5m/0.2m = 25	3m/0.2m = 15	3m/0.4m = 7.5	5m/0.5 = 10
V (m/s) r (m)	$7.8 \times 10^{-6} \text{ 1/r (m)}$	$9.2 \times 10^{-6} \text{ 1/r (m)}$	$1.25 \times 10^{-6} \text{ 1/r (m)}$	$1.08 \times 10^{-6} \text{ 1/r (m)}$
0.5	$1.56 \times 10^{-5}$	$1.84 \times 10^{-5}$	$2.5 \times 10^{-5}$	$2.16 \times 10^{-5}$
1.0	$7.8 \times 10^{-6}$	$9.2 \times 10^{-6}$	$1.25 \times 10^{-6}$	$1.1 \times 10^{-6}$
2.0	$3.9 \times 10^{-6}$	$4.6 \times 10^{-6}$	$6.25 \times 10^{-6}$	$5.4 \times 10^{-6}$
3.0	$2.6 \times 10^{-6}$	$3.1 \times 10^{-6}$	$4.2 \times 10^{-6}$	$3.6 \times 10^{-6}$
4.0	$1.95 \times 10^{-6}$			$2.7 \times 10^{-6}$
5.0	$1.56 \times 10^{-6}$			$2.16 \times 10^{-6}$

use sand as the soil and allow  $\Delta P$  (including the vacuum value at the collector) to be either 10 psi or 20 psi,  $r_d$  to vary between 3 meters and 5 meters, and  $r_o$  to run from 0.2 meters to 0.5 meters. It is seen that over these ranges of field-like parameters, the velocities vary from  $0.78 \times 10^{-6}$  m/s to  $25 \times 10^{-6}$  m/s. The value used in the laboratory experiments (from which  $k$  was derived) was  $83 \times 10^{-6}$  m/s. It will be difficult for logistical reasons, to lower this laboratory value by more than about a factor of ten. Hence we may not be able to determine the chemical removal rates in the laboratory at the needed low steam flow values, more characteristic of the field situation. Nonetheless, we have proceeded to perform experiments in organic chemical removal at various flow rates to determine if there is a strong flow rate dependence. Figure 10 shows the results of rate of removal of kerosene from sand at various flow rates. Figure 11 shows the rate of removal of kerosene from the 50/50 soil at various flow rates.

Before calculating the decontamination time for a given contaminated soil using the model, it is imperative to decide upon the important decontamination parameter. Several obvious choices present themselves.

Is it:

- (a) the absolute volume of steam passed through the soil, i.e., the velocity X time?
- (b) the number of pore volumes of steam passed through the soil, or
- (c) some other unknown parameter?

We must assume a critical parameter before proceeding with the calculation. The data of Figure 11 and 12 favor (b) above. We have the basic experimental data from earlier papers (3,10) with which to determine the decontamination time for a given kerosene spill in the sand/silt soils that we have investigated.

The decontamination time using the critical parameter (a) above is more straightforward than using (b). Assume we have a series of curves such as those presented in Figures 11 and 12. The time for a given percent removal, at a given velocity, can be read directly off the appropriate figure. The velocity as a function of position (i.e., "r") is given by Equation (5). Therefore we can determine the decontamination as a function of time and radial position by Equation (5) and the appropriate decontamination curve. The velocities are higher for smaller r-values (goes as  $1/r$ ).

The calculation of decontamination time using critical parameter (b) above is much more difficult than using concept (a). In the first place the pore volume is not a unique function of  $r$ , because it depends on how thick a layer,  $dr$ , you take for the calculation (see Figure 12). The only possibility is to take the entire pore space of the spill volume and hope that there are compensating factors between the high steam velocity

and short steam dwell time at small "r" and the low velocity, and long dwell time at larger "r". Of course, this can only be answered via experimentation.

It is instructive, even though we don't have a complete set of curves like Figures 10 and 11, to forge ahead and make some estimate of decontamination times. The necessary data are shown in Figures 13 and 14, which give the decontamination rates of kerosene and the flow rate of steam in the various soils. As mentioned previously, the steam flow velocities are  $83 \times 10^{-6}$  m/s in sand and  $13 \times 10^{-6}$  m/s in the 50/50 soil. (These values are based on the volume of condensed steam). By using critical parameter (a) above and assuming the decontamination rate is independent of velocity (this has certainly not been shown experimentally as yet), the values of decontamination times can be read directly from Figure 13 and are shown in Table 3. It must be strongly emphasized that the decontamination times calculated here are certainly on the low side due to the reasons stated in the footnotes to Table 3.

TABLE 3. TIMES FOR DECONTAMINATION USING METHODS (a)  
(i.e., decontamination only depends on time that the steam is passing)

Soil	% Removal	Decontamination Time (minutes)
Sand	60	10
	80	40
	100	100 (extrapolated value)
50 Sand/ 50 Silt	60	300
	80	2800 (extrapolated value)
	100	5300 (extrapolated value)

Note:

The extrapolated values are certainly lower bounds on the decontamination times due to:

- extrapolation of lab data
- the removal rate in the field will probably be smaller the smaller the steam velocity

For critical parameter (b), i.e., the number of pore spaces passed, we must first assume a model of the decontamination area. The "model spill" described earlier (3) will again be utilized. Figure 15 shows the "model spill". It is a kerosene spill in sand (or the 50/50 soil) of pore volume = 40% and covers a circular area of 5 meter radius. The saturation of the kerosene in the originally dry soil is uniform and has a value of 25% (the same as in the lab experiments). The amount of pore volume per meter of length in the spill is

$$\pi(5^2)(1)(0.40) = 31.4 \text{ m}^3 \quad (8)$$

The volume flow rate per unit length in the circular model described earlier is, from Equation (7):

$$\frac{Q}{l} = -2\pi k \frac{\Delta P}{\ln \left( \frac{r_d}{r_o} \right)} \quad (7)$$

The values of  $k\Delta P$  can be obtained from the lab results for the two soils (3,10). The results are:

$$\text{sand: } k\Delta P = 1.76 \times 10^{-5} \frac{\text{m}^2}{\text{s}} \quad (\text{for } \Delta P = 10 \text{ psi})$$

$$50/50: k\Delta P = 0.27 \times 10^{-5} \frac{\text{m}^2}{\text{s}} \quad (\text{for } \Delta P = 15 \text{ psi})$$

Putting these values in Equation (7) with  $r_d = 5 \text{ m}$  and  $r_o = 0.5 \text{ m}$  we obtain:

$$\begin{aligned} \left( \frac{Q}{l} \right)_{\text{sand}} &= \frac{2\pi (1.76 \times 10^{-5})}{\ln 10} \\ &= \frac{2\pi (1.76 \times 10^{-5})}{2.3} \\ &= 4.8 \times 10^{-5} \frac{\text{m}^3}{\text{s}} \quad (\text{this is per meter of length}) \end{aligned}$$

$$\begin{aligned} \left( \frac{Q}{l} \right)_{50/50} &= \frac{2\pi (0.27 \times 10^{-5})}{2.3} \\ &= 0.75 \times 10^{-5} \frac{\text{m}^3}{\text{s}} \quad (\text{this is per meter of length}) \end{aligned}$$

For 100% removal in sand it takes (extrapolated value) about 1000 minutes (see Figure 14). From Figure 14 it is seen that in 1000 minutes about 20,000  $\text{cm}^3$  of steam (condensed) has flowed through the sample. The lab sample has a volume of 456  $\text{cm}^3$  and a pore volume of 178  $\text{cm}^3$ . Therefore 20,000/178 = 112 pore volumes of steam (condensed) must flow through the sample for 100% decontamination. The volume of 112 pore spaces in the field spill is

$$112 (31.4) \text{ m}^3 = 3520 \text{ m}^3$$

Thus the decontamination time for 100% removal is

$$t_{\text{decont.}} = \frac{\text{volume of steam to be passed}}{\text{rate of steam volume passage}} \quad (9)$$

$$\begin{aligned} (t_{\text{decont.}})_{\text{sand}} &= \frac{3520 \text{ m}^3}{4.2 \times 10^{-5} \frac{\text{m}^3}{\text{s}}} \\ &= 7.3 \times 10^7 \text{ s} \end{aligned}$$

$$= 28 \text{ months}$$

Results using the above approach are given in Table 4. Included in the table are results for sand and the 50/50 soil at steam pressures of both 5 psi and 10 psi and various  $r_d$  and  $r_o$  values.

TABLE 4(a). DECONTAMINATION TIMES IN MONTHS, FOR THE TWO SOILS AT THE VARIOUS PARAMETERS

	Sand ( $\Delta P = 10$ psi) removal amount			50/50 Soil ( $\Delta P = 15$ psi) removal amount		
	60%	80%	100%	60%	80%	100%
	(extrapolated)			(extrapolated)		
$r_d = 5$ m						
$r_o = 0.5$ m	0.56	1.4	28	28.5	175	380
$r_o = 0.25$ m	0.73	1.8	36.5	37.2	228	496
$r_o = 0.10$ m	0.95	2.4	47.6	48.5	297	646
$r_d = 3$ m						
$r_o = 0.5$ m	0.44	1.1	21.8	22.2	136	296
$r_o = 0.25$ m	0.60	1.5	30	30.6	188	408
$r_o = 0.10$ m	0.83	2.1	41.4	42.2	259	562
$r_d = 2$ m						
$r_o = 0.5$ m	0.34	0.84	16.8	17.3	106	230
$r_o = 0.25$ m	0.50	1.26	25.2	25.8	158	344
$r_o = 0.10$ m	0.73	1.83	36.6	37.2	228	496

TABLE 4(b). DECONTAMINATION TIMES IN MONTHS, FOR THE TWO SOILS AT THE VARIOUS PARAMETERS

	Sand ( $\Delta P = 15$ psi) removal amount			50/50 Soil ( $\Delta P = 20$ psi) removal amount		
	60%	80%	100%	60%	80%	100%
	(extrapolated)			(extrapolated)		
$r_d = 5$ m						
$r_o = 0.5$ m	0.28	0.7	14	14.2	87.5	190
$r_o = 0.25$ m	0.37	0.9	18.2	18.6	114	248
$r_o = 0.10$ m	0.48	1.2	23.8	24.3	148	323
$r_d = 3$ m						
$r_o = 0.5$ m	0.22	0.56	10.9	11.1	68	148
$r_o = 0.25$ m	0.30	0.75	15	15.3	94	204
$r_o = 0.10$ m	0.42	1.1	20.7	21.1	130	281
$r_d = 2$ m						
$r_o = 0.5$ m	0.17	0.42	8.4	8.7	53	115
$r_o = 0.25$ m	0.25	0.63	12.6	12.9	79	172
$r_o = 0.10$ m	0.37	0.92	18.3	18.6	114	248

#### SUMMARY AND CONCLUSIONS

To be presented at Conference when data acquisition is more complete.

#### ACKNOWLEDGEMENTS

The Drexel authors would like to thank the Risk Reduction Engineering Laboratory of the U.S. Environmental Protection Agency, Edison, New Jersey for support through Cooperative Agreement Number CR 813022.

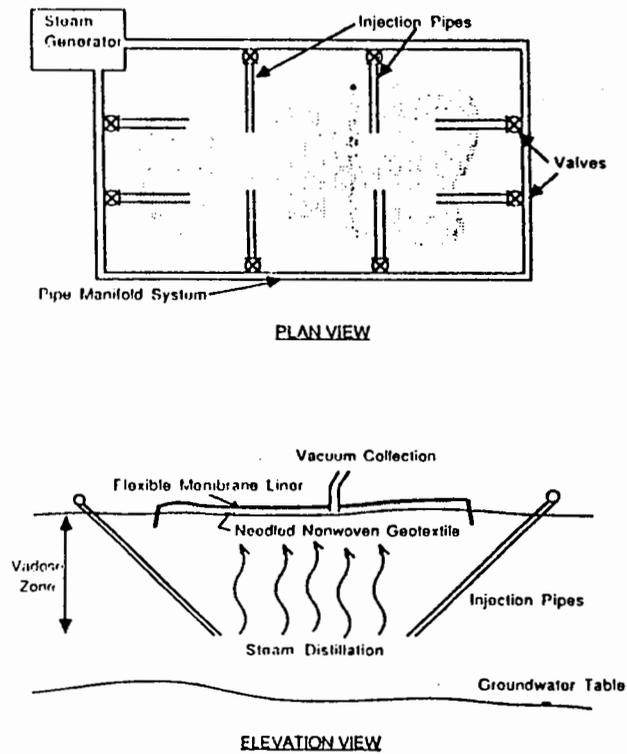


Figure 1 - Schematic diagram of geosynthetic steam collection cap.

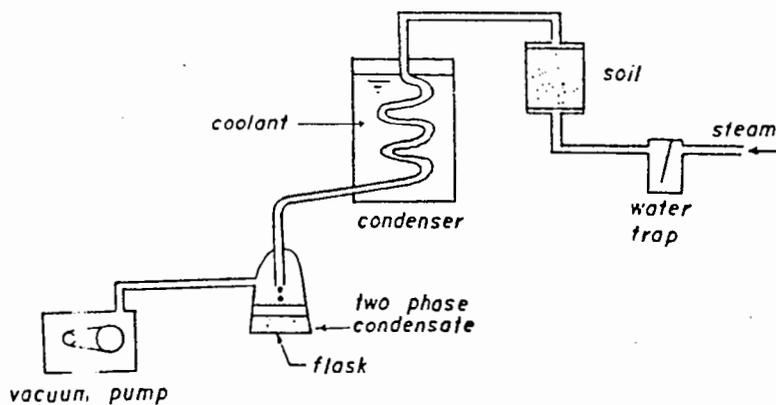


Figure 2 - Schematic diagram of the experimental setup for vacuum-assisted steam stripping studies in the laboratory.

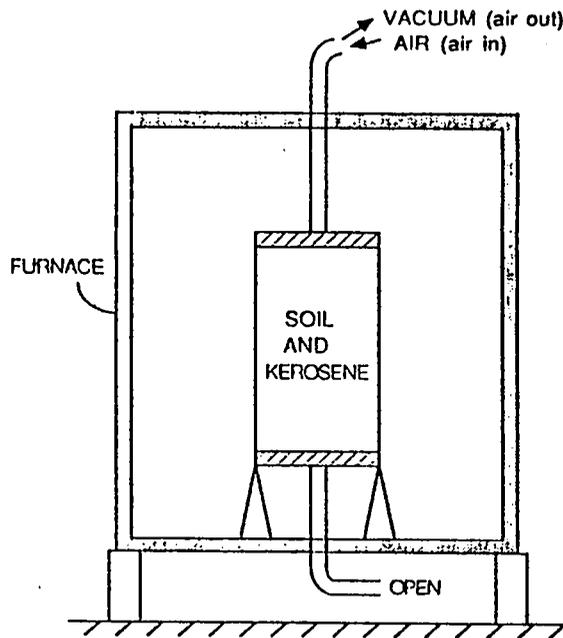


Figure 3 - Schematic diagram of the experimental setup for vacuum extraction studies in the laboratory.

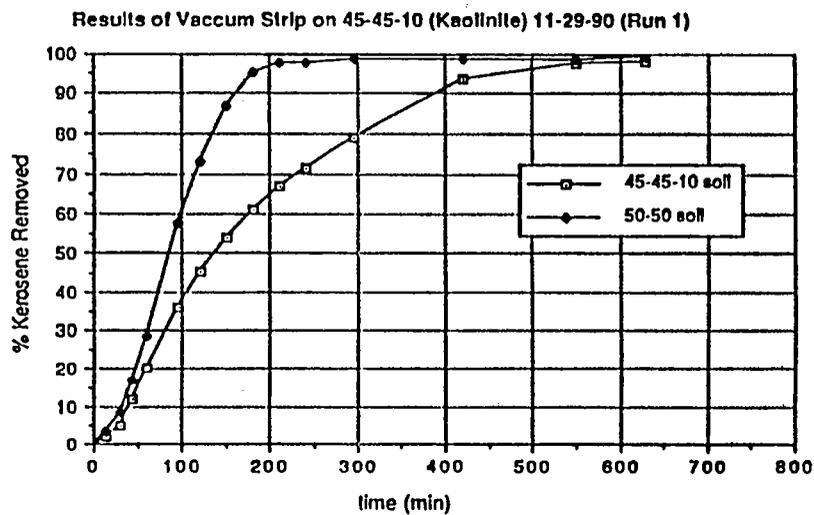


Figure 4 - Results for vacuum stripping of kerosene from a 50 sand/50 silt soil and from a 45 sand/45 silt/10 kaolinite soil (soil temperature = 100°C)

Vacuum Strip of Sand /Silt / Clay Fraction (1st. series)

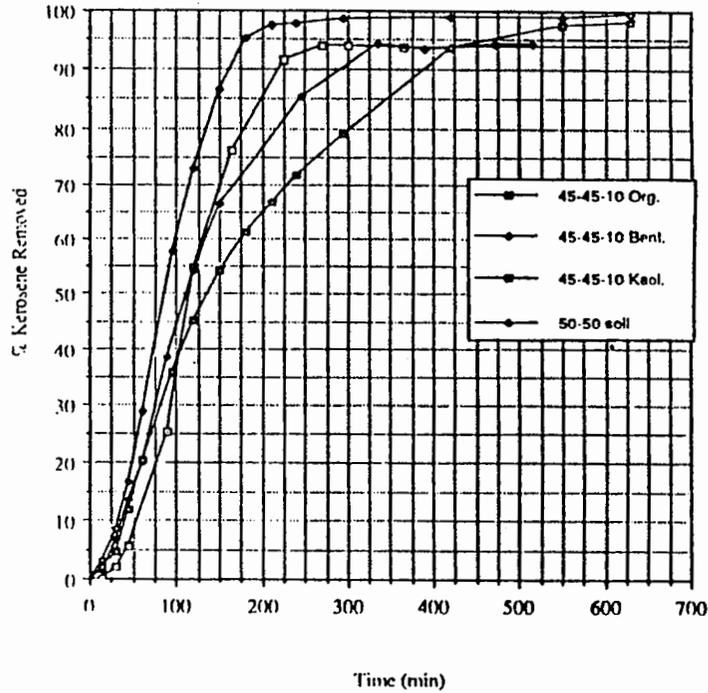


Figure 5 - Results for vacuum stripping of kerosene from various sand/silt/clay or sand/silt/organic mixtures (soil temperature = 100°C)

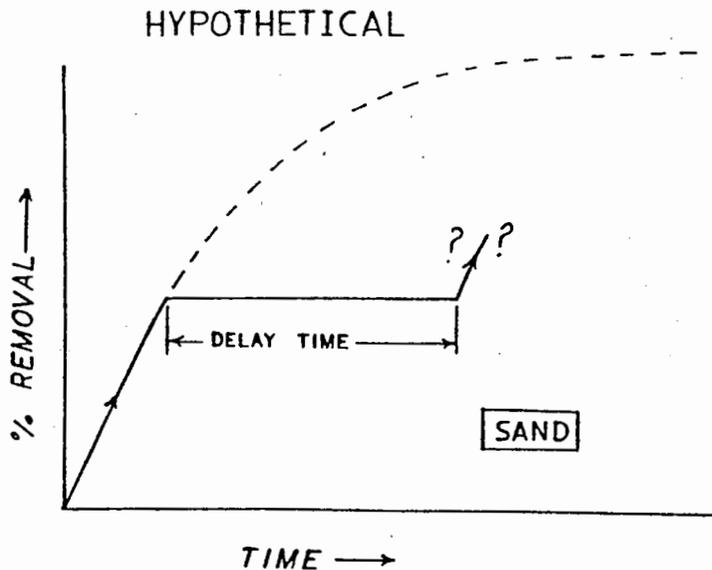


Figure 6 - Hypothetical delay time data in sand. (THIS IS NOT ACTUAL DATA!)

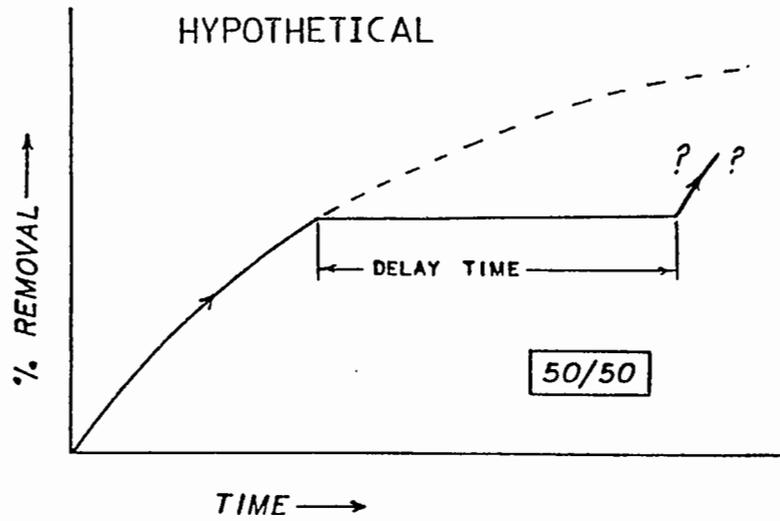


Figure 7 - Hypothetical delay time data in the 50/50 soil.  
(THIS IS NOT ACTUAL DATA!)

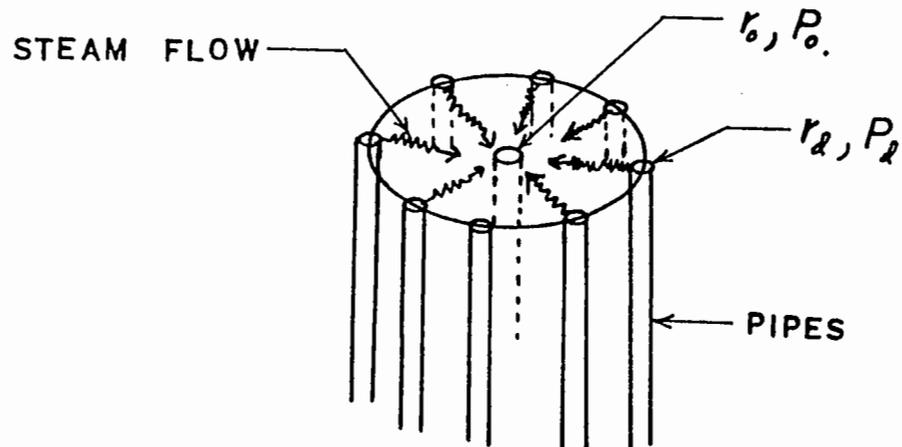


Figure 8 - The circular-symmetry model for the analytical theory calculations for soil decontamination times using vacuum-assisted steam stripping.

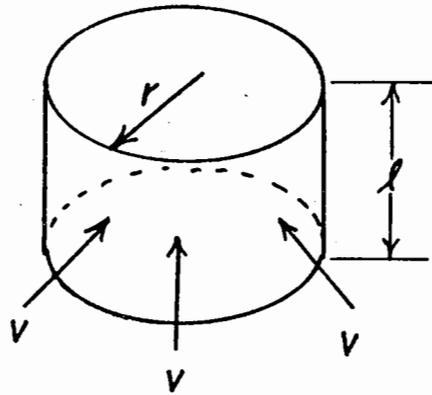


Figure 9 - Steam flow through a lateral surface area.

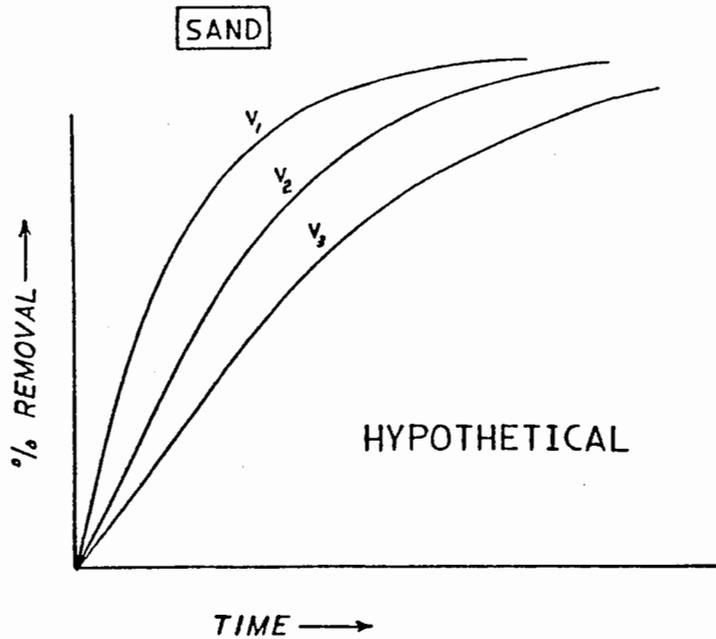


Figure 10 - Hypothetical data for steam stripping removal efficiency in sand for various steam flow velocities. (THIS IS NOT ACTUAL DATA!)

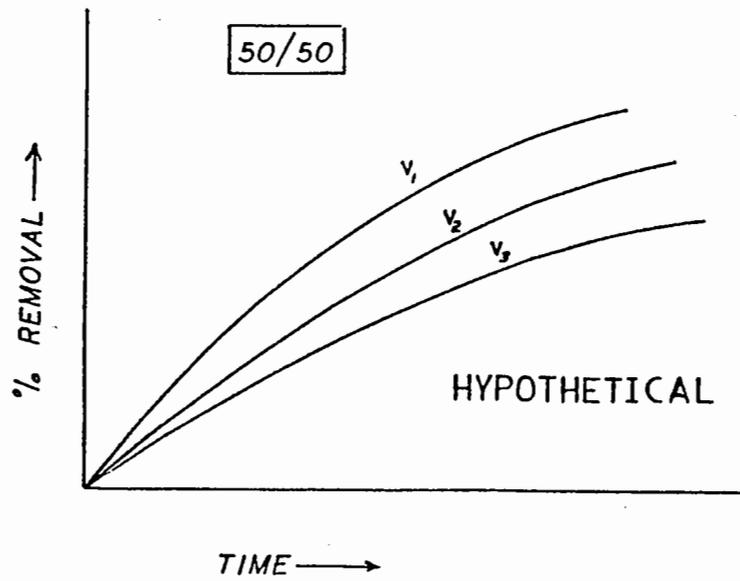


Figure 11 - Hypothetical data for steam stripping removal efficiency in the 50/50 soil for various velocities.  
(THIS IS NOT ACTUAL DATA!)

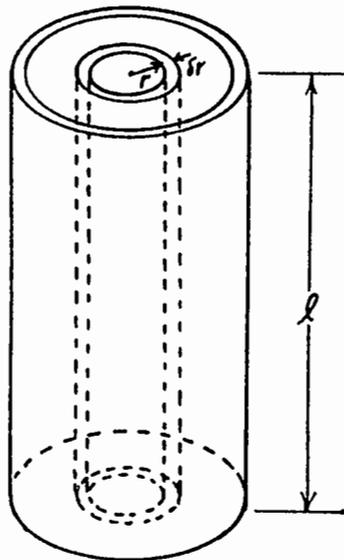


Figure 12 - Diagram showing different volumes present in cylindrical shells. ( $V = 2\pi r l dr$ )

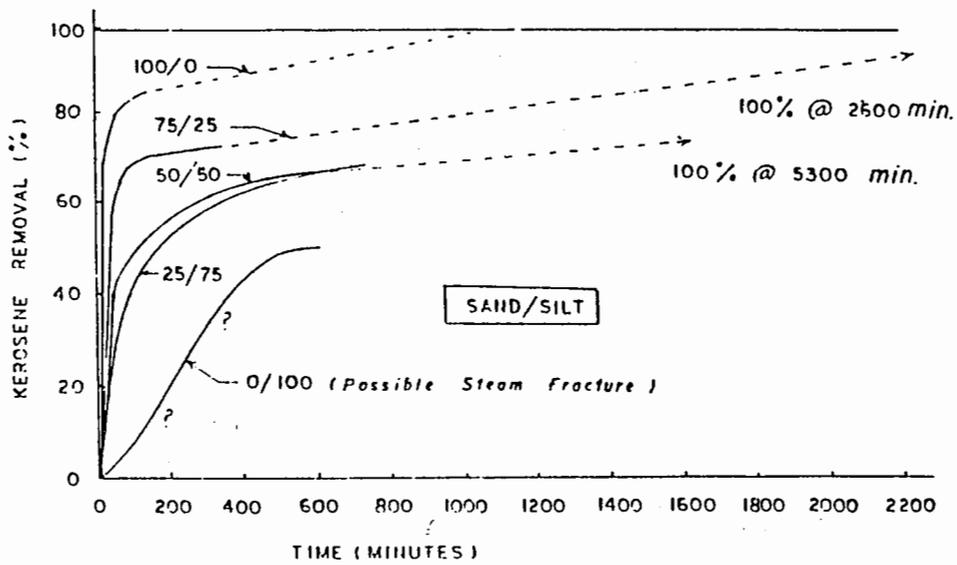


Figure 13 - Kerosene removal efficiency in the various sand/silt mixtures. (These data apply for only one steam flow velocity for each soil).

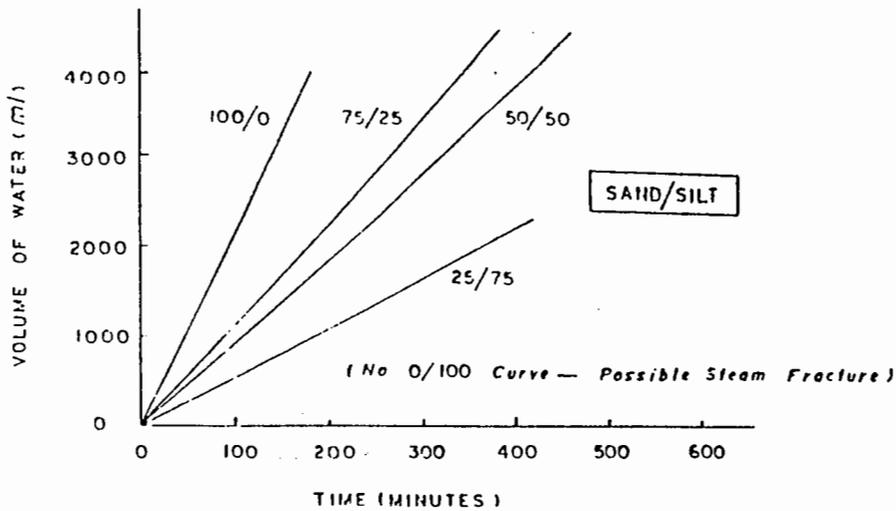


Figure 14 - Steam volume flow rate for the various sand/silt mixtures.

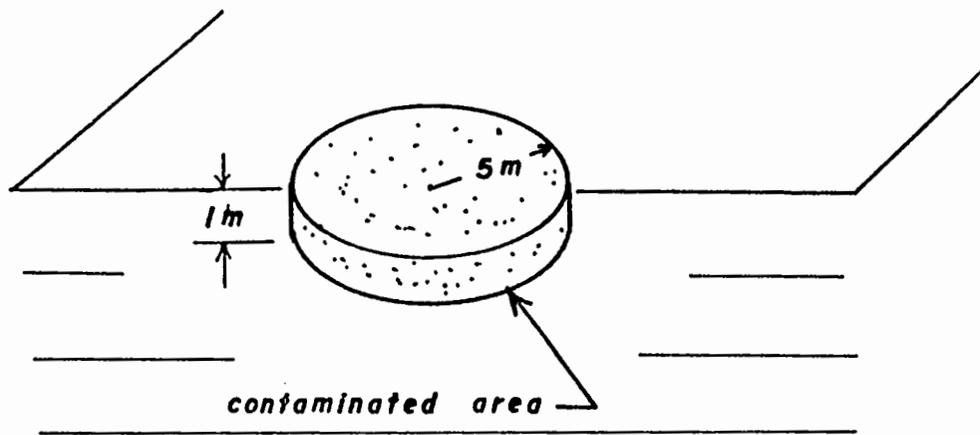


Figure 15 - Schematic diagram of assumed kerosene spill volume.

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EFFECTIVENESS OF COMMERCIAL MICROBIAL PRODUCTS IN ENHANCING OIL DEGRADATION IN  
PRINCE WILLIAM SOUND FIELD PLOTS

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ABSTRACT

In the spring of 1990, previously reported laboratory experiments were conducted on 10 commercial microbial products to test for enhanced biodegradation of weathered crude oil from the *Exxon Valdez* oil spill. The laboratory tests measured the rate and extent of oil degradation in closed flasks. Weathered oil from the beaches in Alaska and seawater from Prince William Sound were used in the tests. Two of the 10 products were found to provide significantly greater alkane degradation than flasks supplemented with mineral nutrients alone. These two products were selected for further testing on a beach in Prince William Sound.

A randomized complete block experiment was designed to compare the effectiveness of these two products in enhancing oil degradation compared to simple fertilizer alone. Four small plots consisting of a no nutrient control, a mineral nutrient plot, and two plots receiving mineral nutrients plus the two products, were laid out on a contaminated beach. These four plots comprised a "block" of treatments, and this block was replicated four times on the same beach. The plots were positioned in random order within each block. Triplicate samples of beach sediment were collected at four equally spaced time intervals and analyzed for oil residue weight and alkane hydrocarbon profile changes with time. The objective was to determine if either of the two commercial microbiological products was able to enhance bioremediation of an oil-contaminated beach in Prince William Sound to an extent greater than that achievable by simple fertilizer application. Results indicated no significant differences among the four treatments in the 27-day time period of the experiment.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

### BACKGROUND

The largest field bioremediation test ever attempted was conducted by the U.S. Environmental Protection Agency and the Exxon Corporation on the shorelines of Prince William Sound, Alaska, following the oil spill from the supertanker *Exxon Valdez* in March, 1989 (1). In that study, investigators concluded that application of nitrogen and phosphorus nutrients enhanced biodegradation of the crude oil. Furthermore, no adverse environmental effects were observed as a result of the fertilizer application.

Other studies have met with mixed success. In February 1970, the tanker *Arrow* spilled approximately 108,000 barrels of bunker C oil into Chedabucto Bay, Nova Scotia. Rashid (2) reported 3.5 years later substantial losses of *n*-alkanes resulting largely from microbial degradation, aided by the wave-driven mixing permitting infusion of dissolved oxygen and exogenous nutrients. Cretney *et al.* (3) reported that biodegradation accounted for almost complete removal of *n*-alkanes during the first year after the tanker *Irish Stardust* ran aground near Vancouver Island, B.C. In contrast, Colwell *et al.* (4) observed prolonged persistence of oil spilled from the tanker *Metula* in the Straits of Magellan in 1978. They attributed the slow biodegradation rates not to the cold temperatures typical of the area but to the limited concentration of nitrogen and phosphorus available in the seawater, as well as restricted accessibility to degradable compounds within aggregated oils or tar balls. Atlas *et al.* (5), after experimentally contaminating a coastal Arctic ecosystem with Prudhoe Bay crude oil, measured low rates of natural hydrocarbon biodegradation. They found that temperature and availability of nutrients limited the biodegradation rate. Several research teams investigated the fate of the *Amoco Cadiz* crude oil spilled off the Brittany Coast in 1978 (6-11). Microbial degradation was found to have played a crucial role in the weathering of the oil contaminating the shoreline in the intertidal zone. There were rapid changes in the *n*-alkane/isoprenoid hydrocarbon ratios within weeks following the spill. The isoprenoid alkanes, *n*-alkanes with carbon number C<sub>27</sub> to C<sub>31</sub>, hopanes, alkylated dibenzothiophenes, and alkylated phenanthrenes were the classes of compounds most resistant to biodegradation.

Another way to enhance bioremediation in the field is inoculation with allochthonous microorganisms. Cultures and cultural products have been added to different environments to stimulate biological removal of contaminants. Some of the studies have demonstrated enhancement, while others have not (12). In a recent study, Dott *et al.* (13) compared fuel oil degradation rates of activated sludge microorganisms with nine different commercial bacterial cultures in separate laboratory flasks. They found that the rate and extent of *n*-alkane and total hydrocarbon degradation by the diverse populations in activated sludge were significantly higher than any of the highly adapted commercially available cultures. Lehtomaki and Niemela (14) found that addition of brewers' yeast to oil-contaminated soil enhanced oil removal 2- to 10-fold. This was most likely due to the supply of critical nutrients, vitamins, or cofactors that were naturally deficient in the soil. Christianson and Spraker (15) reported a series of case histories of refinery wastewa-

ter treatment plants using commercial cultures to overcome various specific problems, such as foaming, toxic loads, low biomass, etc. Most success with biodegradation enhancement by allochthonous microbial cultures has been achieved when chemostats or fermentors were used to control conditions or reduce competition from indigenous microflora (16) .

Venosa *et al.* (17) recently conducted laboratory tests on 10 commercial products for microbial degradation of weathered crude oil from the *Exxon Valdez* spill. The products were selected from a public solicitation by EPA and review of proposals by a panel of experts convened by the National Environmental Technology Applications Corporation (NETAC), a non-profit organization dedicated to the commercialization of environmental technologies. Laboratory tests on the products were conducted to measure the rate and extent of oil degradation in closed ecosystems. Weathered oil from the beaches in Alaska and seawater from Prince William Sound were used in the tests. The NETAC panel reviewed the results of the tests and agreed with the recommendation for further testing of two products that exceeded the performance of inorganic nutrient addition. This paper presents the results of the field testing of the two selected products. The objective was to determine if commercial microbiological products were able to enhance bioremediation of an oil-contaminated beach in Prince William Sound to an extent greater than that achievable by simple fertilizer application. The two companies that participated in the testing were Sybron, Inc. and ERI-Waste Microbes, Inc.

#### MATERIALS AND METHODS

##### PLOT DESCRIPTION

A schematic representation of the experimental layout is depicted in Figure 1.

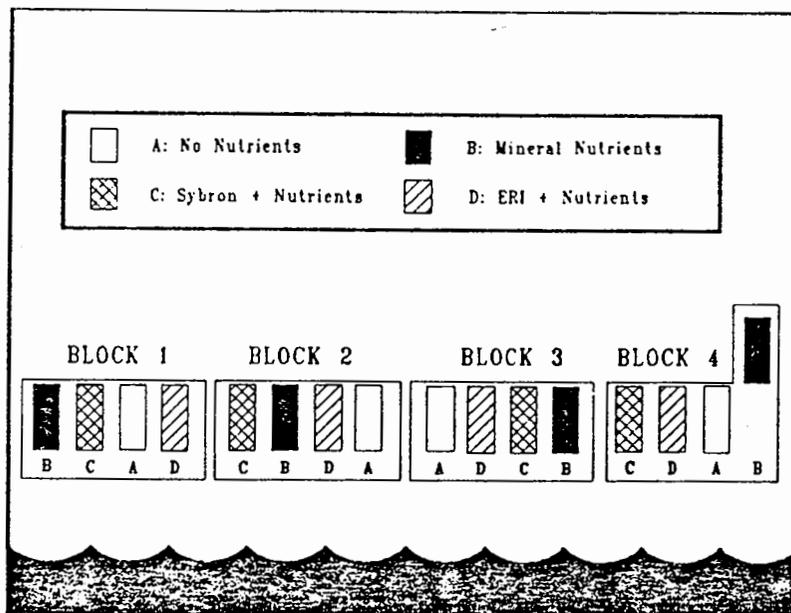


Figure 1. Randomized Complete Block Design Showing Location of Replicate Plots at Disk Island.

The experiment was a randomized complete block design. Four beach segments ("blocks"), each 20 m wide (labeled 1 through 4) were staked out in the intertidal zone at Disk Island (designated DI-67A), an island in Prince William Sound located between Eleanor and Knight Islands. Within each block were 4 treatment plots, labeled A through D, 2 m wide by 5 m long (top-to-bottom). The plots were separated from each other by a buffer zone measuring 3 m in width. Plot A, color-coded blue on the shoreline, was the no-treatment control. Plot B, color-coded orange, was the nutrient-only treatment. Plot C, color-coded green, was the plot receiving nutrients plus Sybron's product. Plot D, color-coded red, was the plot receiving nutrients plus ERI's product. The treatment plots within each block were randomly distributed according to the following scheme: block 1, BCAD; block 2, CBDA; block 3, ADCB; and block 4, CDAB.

Each of the 16 plots was subdivided horizontally into three equal segments 2 m wide by 1.67 m long, as shown schematically in Figure 2.

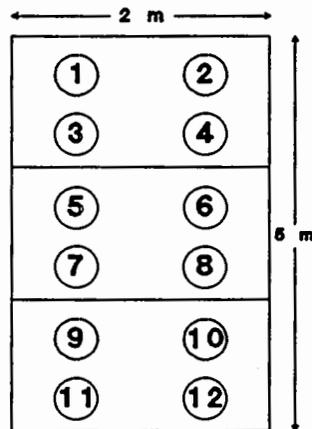


Figure 2. Typical Plot Showing Location of Sampling Bags.

In each of the three segments, four bags, each made of fiberglass screening material and containing approximately 750 to 1000 g of uniformly sized oily gravel, were buried approximately 5 to 10 cm below the surface and covered with mixed sand and gravel. The four bags corresponded to the four sampling events that were planned for the experiment. A surveyor's ribbon was attached to each bag for easy identification. The 12 samples within each block were numbered 1 through 4 in the top third, 5 through 8 in the middle third, and 9 through 12 in the bottom third.

The bags had previously been filled with gravel that had first been sieved through a 25 mm coarse screen to remove large stones and then a 4.75 mm sieve to remove the small sand granules that compact the beach material. The gravel was mixed manually by shovels and hoes in a large wooden container to

achieve reasonable homogeneity with respect to oil contamination and rock size. These bags served as samples to be taken on the appropriate sampling days.

#### SAMPLING

On a given sampling day, triplicate samples from each plot within a block were collected according to a random schedule. One sample was randomly taken from each of the three identical sectors of each plot. Some of the gravel was poured into 500 mL I-Chem jars, labeled, and placed in a cooler to be carried back to Valdez for freezing and shipment via Federal Express to the analytical chemistry laboratory located in Pittsburgh, PA. The rest of the gravel was archived in aluminum foil and frozen. Thus, 48 samples were collected on each of the four sampling days, giving a total of 192 samples for the entire experiment.

#### SEDIMENT CHEMISTRY

The 48 samples were analyzed for oil residue weight by methylene chloride extraction followed by evaporation to dryness and weighing on an analytical balance. After weighing, each sample was reconstituted with methylene chloride, passed through a silica gel fractionation column, and analyzed for the normal alkanes C12 through C34 plus the isoprenoid hydrocarbons pristane and phytane by gas chromatography using a flame ionization detector. The aliphatic fraction was eluted from the silica gel column with hexane prior to GC injection.

#### MICROBIOLOGY

Subsamples from the 8 plots of blocks 2 and 3 were analyzed for oil degrading bacteria by standard plate count, using Bushnell-Haas medium supplemented with Prudhoe Bay crude oil as the carbon source. Only one of the three triplicates from those 8 plots was analyzed for microbial numbers. The plates were incubated at 15°C for 21 days and the colonies counted.

#### NUTRIENTS

Within 8 of the 16 plots on the shoreline, a well was installed for collecting nutrient samples. Two wells extending approximately 60 cm below the surface were driven into each of the four blocks, one in the no-nutrient control plot and one in the nutrient-treated plot. Subsurface water from these 8 wells served as samples for nutrient analysis.

#### APPLICATION OF NUTRIENTS

The source of nitrogen was ammonium nitrate. Each 2 m x 5 m plot received 200 g of N ( $20 \text{ g/m}^2$ ). At 35% N, the amount of  $\text{NH}_4\text{NO}_3$  containing 200 g of N was 570 g or 1.25 lb per plot. This amount, less approximately 40 g to account for the N in the product containing the phosphate salt (see next paragraph), was added to 6 gallons of seawater and the contents stirred until dissolved. A 2-gallon plastic sprinkling can was filled with the solution and

the entire contents poured onto the top third of a plot earmarked for nutrients. The sprinkling can was again filled and the contents poured onto the middle third. The procedure was repeated for the bottom third.

The source of phosphorus was an Ortho product named "Upstart," which had an N-P-K analysis of 3-10-3. At 10% P<sub>2</sub>O<sub>5</sub>, the amount of Upstart used was 450 g (1 lb) per plot. This corresponded to a phosphorus loading of 20 g P per plot (2 g P/m<sup>2</sup>). The 450 g of Upstart was added to the 6 gallons of seawater above (after the NH<sub>4</sub>NO<sub>3</sub> had been dissolved) before applying to each plot. Note that this product contained 3% N in the form of NH<sub>4</sub>NO<sub>3</sub>. The amount of N in Upstart had already been accounted for in the above 530 g computation of NH<sub>4</sub>NO<sub>3</sub> needs.

## SCHEDULE

The entire experiment lasted only 27 days because severe Alaskan winter weather precludes field activities beyond the month of August. Day 0 occurred on Sunday, July 29, 1990. Nutrients and commercial products were applied on days 0, 4, 8, 12, 16, 20, and 24. One extra application day, day 2, was used for an additional commercial product application, as specified by the two vendors. After nutrients and products had been delivered to the appropriate plots, randomly assigned triplicate sampling bags were removed from the plots for time 0 sediment chemistry and microbiology analysis. The other triplicate sampling bags were collected on days 9, 18, and 27. Nutrient sampling took place on days 1, 2, 3, 4, 17, 18, 19, and 20. This allowed determination of nutrient concentrations throughout the four-day interval between applications at two different times in the experiment.

## RESULTS

### PERSISTENCE OF NUTRIENTS

Figures 3-5 summarize the average changes in nutrient levels with time in each block on Disk Island. Figure 3 shows the ammonia-N data, Figure 4 the nitrate-N data, and Figure 5 the phosphate-P data.

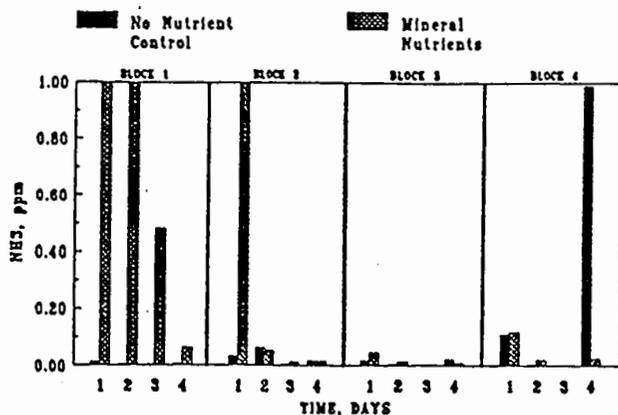


Figure 3. Changes in NH<sub>3</sub>-N in each block within 4 days after application.

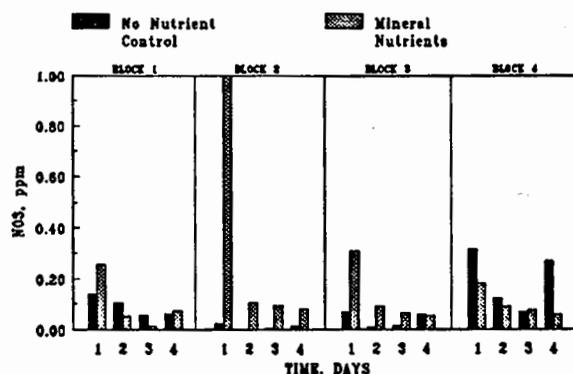


Figure 4. Changes in NO<sub>3</sub>-N in each block within 4 days after application.

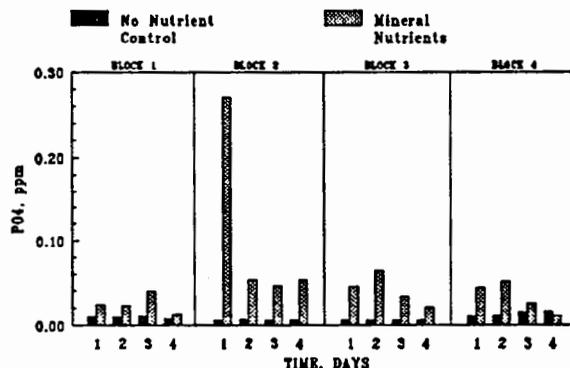


Figure 5. Changes in PO<sub>4</sub>-P in each block within 4 days after application.

Persistence of ammonia-N was the most erratic. In block 1 the levels of NH<sub>3</sub>-N in the nutrient-treated plot were measured at 4.0 and 1.1 mg/L one and two days after application, respectively, and in block 2 the NH<sub>3</sub>-N was 1.7 mg/L one day after application. Little NH<sub>3</sub>-N was measured in any of the control plots at any time except in block 4, where 0.1 mg/L was measured after one day and almost 1.0 mg/L after four days. The source of the high NH<sub>3</sub>-N spike in the control plot of the fourth block may have been caused by carry-over of nutrients from the nutrient-treated plot onto the control plot. The nutrient-treated plot had to be placed above the control plot (see Figure 1) because of the presence of compacted peat on the extreme right end of the

beach. There was a surface flow of water from a saltwater lagoon located approximately 50 m above the test area that flowed across the nutrient-treated plot onto the control plot. This stream was not noticed when the plots were first laid out. Although this explains the higher levels of  $\text{NH}_3\text{-N}$  measured one day after application, it does not explain why such a high spike was observed on the fourth day.

The nitrate and phosphate data indicate significant but decreasing levels of nutrients in the nutrient-treated plots as time progressed to four days after application (Figures 4 and 5). Again, high levels of  $\text{NO}_3\text{-N}$  and measurable levels of  $\text{PO}_4\text{-P}$  appeared in the control plot of the fourth block four days after application.

#### CHANGES IN OIL DEGRADERS

Oil degrader counts in all plots of blocks 2 and 3 are shown in Figure 6. Although the levels of oil degraders were high in each of the plots, there were no significant changes or differences in any of the plots after 27 days of field testing.

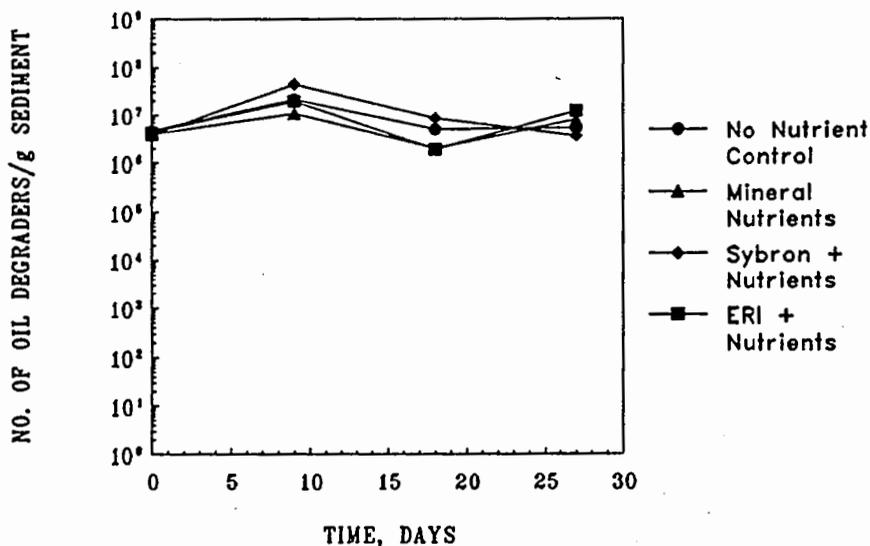


Figure 6. Changes in Oil Degradation Counts on All Plots of Blocks 2 and 3.

#### OIL RESIDUE WEIGHT

Changes in oil residue weight, averaged over all four blocks, are summarized in Figure 7 as a function of time. The hatched bars are the mean residue weights for each of the four treatments, and the error bars depict one

standard deviation unit above and below the means. These error bars represent the variation in oil residue weight among the four blocks and are indicative of the overall experimental error.

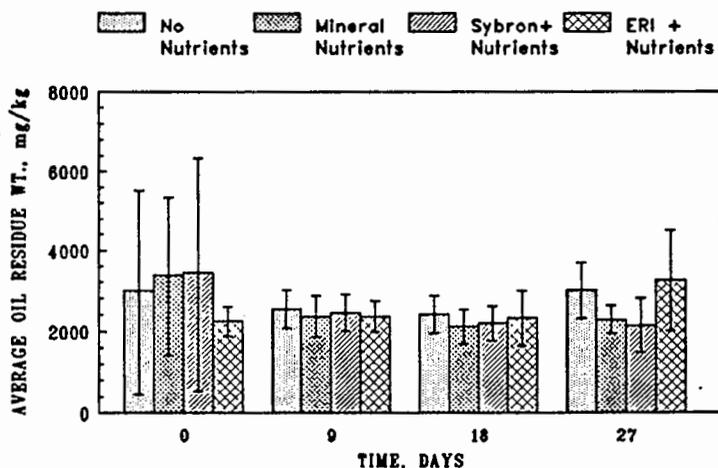


Figure 7. Average Oil Residue Weights for All Treatments.

Visual inspection of the data from the plots treated with mineral nutrients alone and mineral nutrients supplemented with Sybron's product indicates a decrease in oil residue of approximately 33% at the end of the experimental period compared with no net change in the no-nutrient control plot and a slight increase in the ERI plot. When the data were subjected to analysis of variance, however, there were no statistically significant differences among any of the four treatments at the 5% significance level. This was true even after the data were log transformed to stabilize the variance.

Note the broad error bars on Figure 7 at the day 0 sampling time compared with the other three sampling times. Despite the effort to control the heterogeneity of rock size and contamination by the sieving and mixing techniques prior to start-up, there was still substantial variation in oil residue weight from plot to plot and block to block at day 0. To ascertain the source of this variation, a breakout of plot oil residue weights by block was conducted. Results are shown in Figure 8.

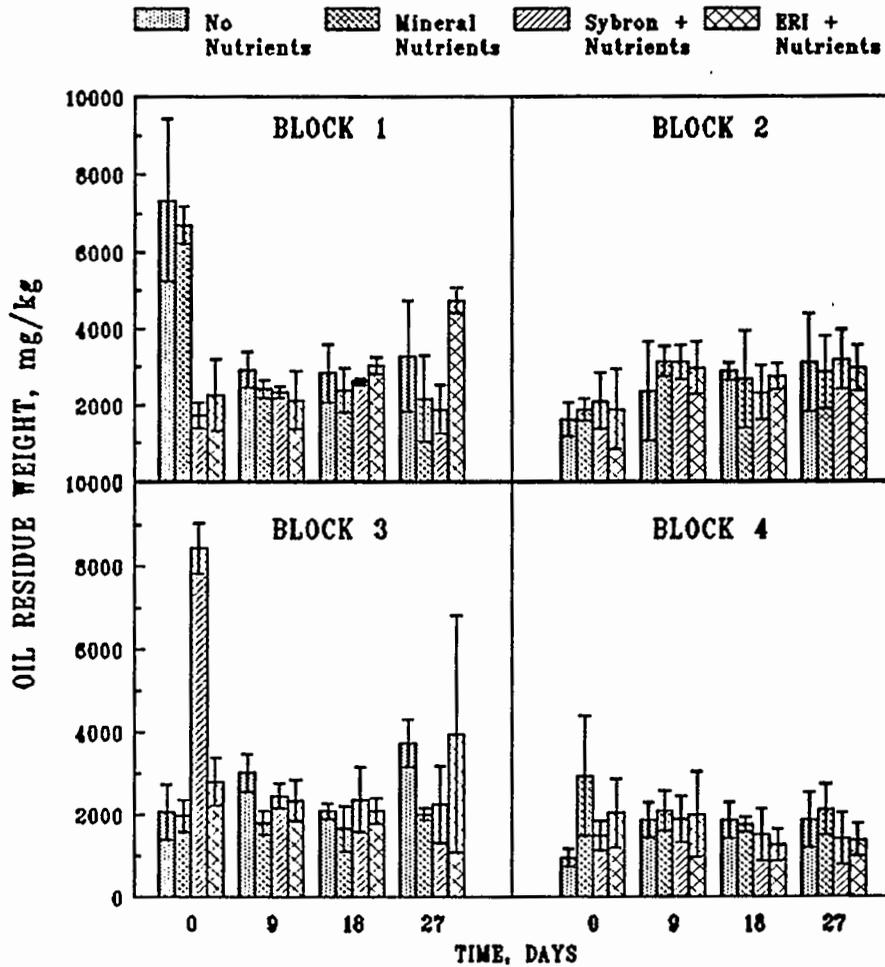


Figure 8. Oil Residue Weights for All Treatments Broken Out by Block.

Examination of these data reveals the differences in the distribution of oil from plot to plot. The error bars shown on this figure are the standard deviations of the triplicate samples within each plot and are indicative of the sampling error. At day 0 the agreement of the triplicate samples averaged within each plot (Figure 8) is better than the agreement of identical plots averaged over blocks (Figure 7). This suggests that the cause of the variation among plots was consistent within each of the plots.

## TOTAL RESOLVABLE ALKANES

All samples were subjected to GC analysis to determine the changes in the aliphatic profiles of the oil among the various treatments. The concentrations of all the normal alkanes and the isoprenoid alkanes pristane and phytane resolvable by GC/FID were summed together for each treatment, averaged over all four blocks, and plotted as a function of time. The data with associated error bars are shown on Figure 9.

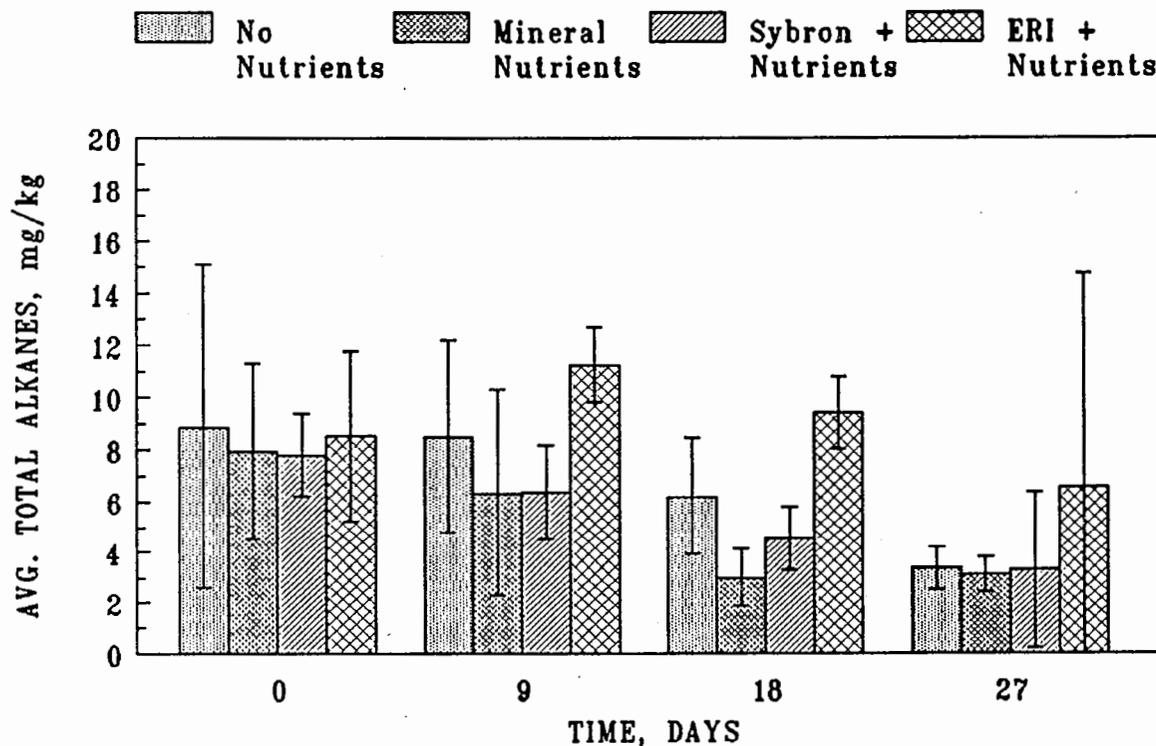


Figure 9. Average Total Resolvable Alkanes for All Treatments.

Except for the day 0 data, the error bars in Figure 9 are generally higher than the corresponding residue weight error bars (Figure 7). Although a downward trend in resolvable alkanes is perceptible after 27 days among all treatments, the analysis of variance revealed no significant differences among the treatments ( $p < 0.05$ ). This agrees with the findings of no significance among treatments in the oil residue weight data.

Figure 10 was constructed to examine the behavior of the GC data among the individual plots within each block. The error bars represent the sampling error associated with the triplicate samples in each plot.

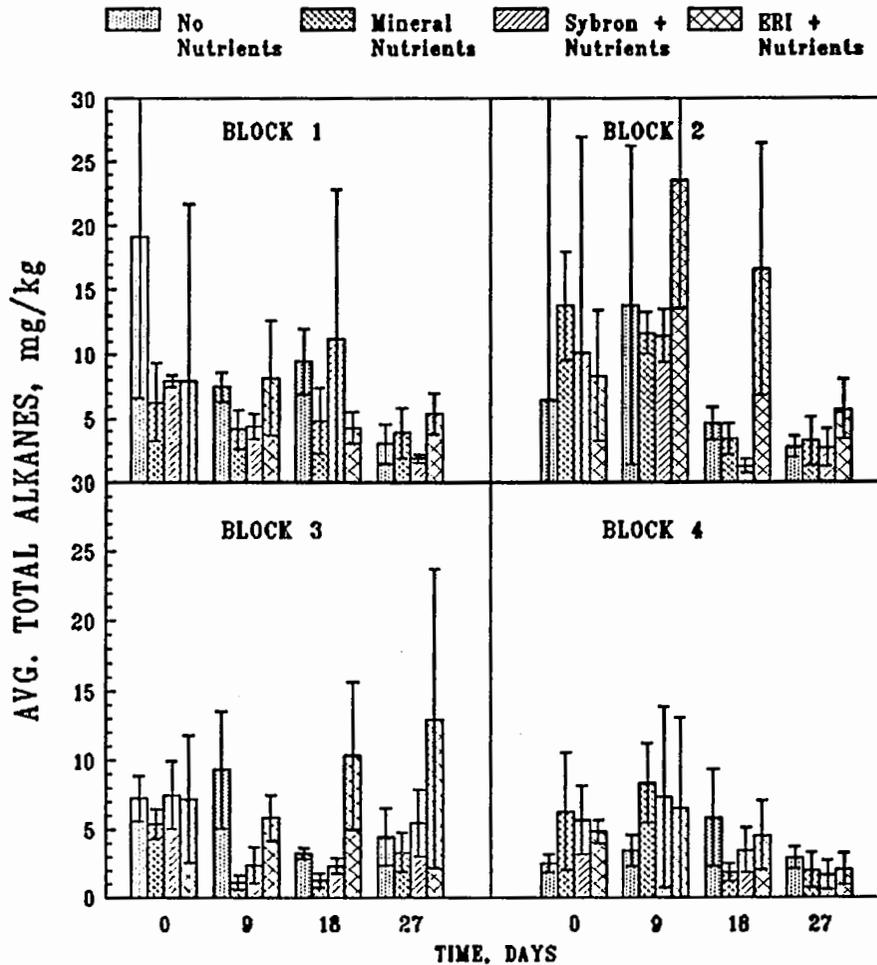


Figure 10. Total Resolvable Alkanes for All Treatments Broken Out by Block.

The error bars are higher overall than the corresponding oil residue weight data (Figure 8). The sampling errors associated with the GC data appear to be no better than the overall experimental error, which contrasts somewhat with the residue weight data.

## N-NONADECANE

To determine if an individual alkane hydrocarbon exhibited biotransformation differences among treatments, the data from a representative normal alkane, n-nonadecane (n-C19), were analyzed in several different ways. First, if n-C19 were biotransformed at the same rate as the total resolvable alkane hydrocarbons, one would expect to see no net change with time when the n-C19/total alkane ratio was plotted. Figure 11 summarizes such a plot.

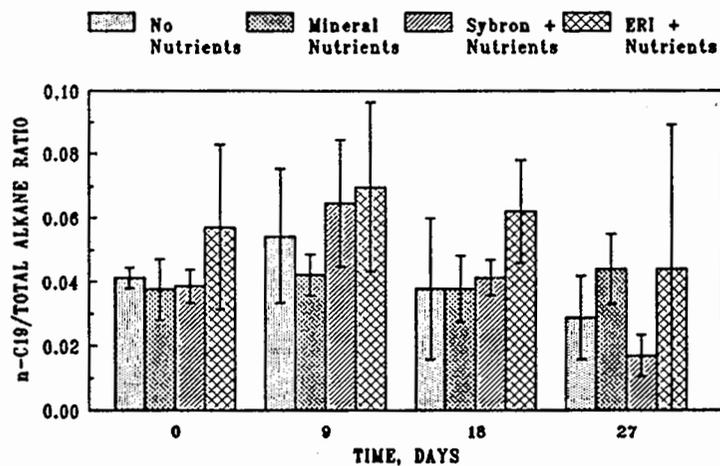


Figure 11. Average n-C19/Total Alkane Ratio for All Treatments.

No significant changes are evident among the treatments within 27 days.

Second, if n-C19 were biotransformed in the same way as the total resolvable alkanes, one would expect to observe the same behavior in the n-C19/residue weight ratio as the total alkane/residue weight ratio. Figures 12 and 13 show that this is the case.

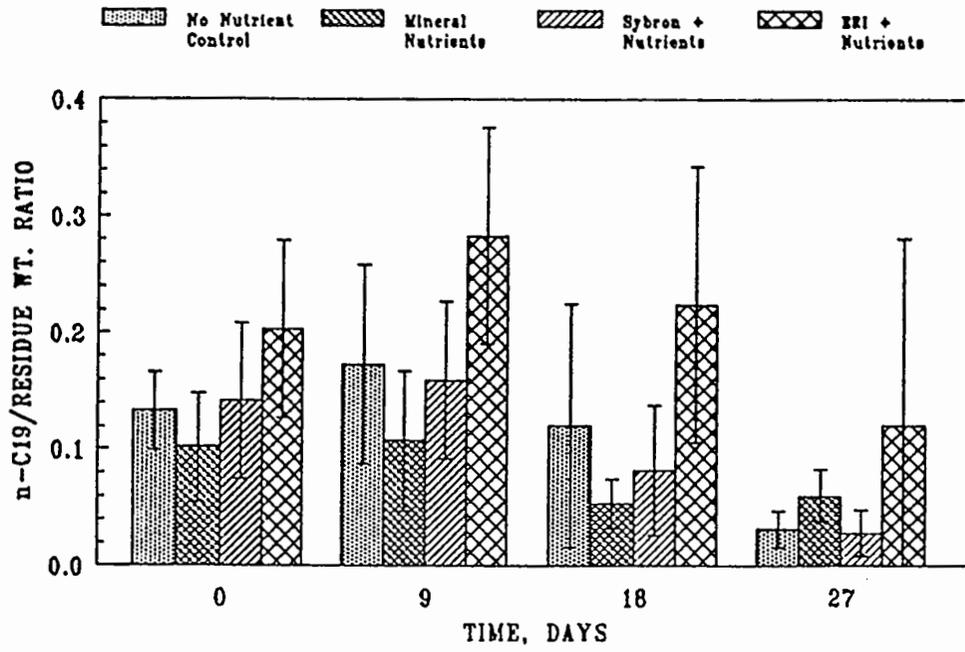


Figure 12. Average n-C19/Residue Weight Ratio for All Treatments.

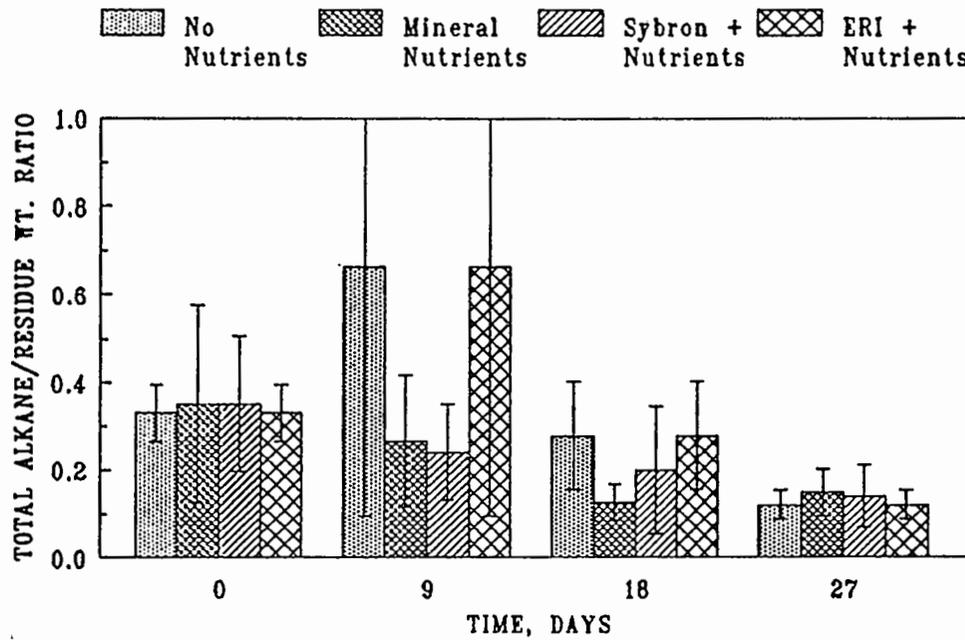


Figure 13. Average Total Alkane/Residue Weight Ratio for All Treatments.

Thus, whether one examines the total alkane hydrocarbon fraction of the oil or a representative normal alkane within it, the results are the same: no enhancement either by nutrients alone or by nutrients supplemented with commercial inocula.

One important observation from Figure 13 is the magnitude of the total alkane/residue weight ratio. The sum total alkane hydrocarbons resolvable by GC/FID are less than 0.5% of the total oil residue weight 1.5 years after the *Exxon Valdez* spill. This is the most likely explanation for the lack of enhancement of bioremediation by either nutrient addition alone or nutrient addition supplemented with commercial microbial cultures. Over 99.5% of the oil remaining on Disk Island 1.5 years after the spill is not resolvable by conventional gas chromatography. The compounds comprising this recalcitrant fraction are likely the tars and asphaltines that will only slowly degrade with time. The 27-day period of this investigation was much too short to determine if enhancement of bioremediation is possible.

## DISCUSSION

The conclusions reached in this field study were based on three sources of information: nutrient persistence, microbiology, and sediment chemistry. The nutrient data clearly demonstrated that nitrogen and phosphorus persisted at measurably higher levels in the treated plots compared with the control plots throughout the four days between applications. These measurements were taken approximately 60 cm below the surface of the beach, suggesting that nutrients were in constant contact with the subsurface sediment layers for relatively long periods of time.

The microbiology data clearly demonstrated no net increase in oil degrader populations in any of the plots after 27 days and no differences among the four treatments at any time during the 27 day period. The oil degrader populations were high to begin with and were maintained with or without the presence of excess nutrients. Either the oil degraders were dormant or, more likely, they were sufficiently able to sustain their activity with the oligotrophic levels of nutrients present in the ambient environment.

Sediment chemistry revealed the most definitive information, because it was the basis of the statistical analyses conducted. No significant differences were found among the four treatments at the 5% significance level either from the standpoint of oil residue weight, total resolvable alkane hydrocarbons, *n*-C19/total alkane ratio, *n*-C19/residue weight ratio, or total alkane/residue weight ratio. The experimental error from the residue weight data was higher than the sampling error, which clearly points out the necessity to replicate treatments when conducting field experiments.

An instructive piece of information obtained from this investigation was the fact that most of the readily biodegradable compounds in the aliphatic fraction of the contaminating oil has disappeared in the 1.5 years since the spill took place off Bligh Reef in Prince William Sound. This is the most likely explanation for the lack of any significant enhancement observed in the short time period allotted for this study. Further evidence supporting this conclusion derives from examining the *n*-alkane/isoprenoid alkane ratios.

These ratios have been used in past literature to indicate extent of biodegradation; the lower the ratio, the more extensive the biodegradation. The average *n*-C17/pristane and *n*-C18/phytane ratios on day 0 for all the plots on Disk Island were 0.18 and 0.27, respectively. This compares with approximately 1.5 to 1.8 for unweathered Prudhoe Bay crude oil. Thus, the remaining oil present on Disk Island will likely degrade very slowly from now on because of the recalcitrant nature of the substrate. If either nutrient application or commercial inoculation can accelerate this rate, the time period must extend significantly beyond the 27 days allotted for this study or the trial must be conducted on beaches with fresher oil contamination.

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BIODEGRADATION OF VOLATILE ORGANIC COMPOUNDS IN AEROBIC AND  
ANAEROBIC BIOFILTERS

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ABSTRACT

Biodegradation is an attractive alternative for the treatment of volatile organic compounds (VOCs) present in landfill leachates. A stripper-biofilter system can be used to control the air pollution due to these VOCs. Preliminary experimental results on the stripping of volatiles from landfill leachate streams and their biodegradation in aerobic and anaerobic biofilters are presented in this paper. This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

In recent years, emission of volatile organic compounds (VOCs) has received increased attention from EPA, OSHA and other government agencies due to the serious human health hazards these compounds present as pollutants. The origins of these VOCs can be from manufacturing process or wastewater treatment plants, where the waste stream is stripped of the VOCs during aeration. Another significant source of these pollutants is from landfill leachate. Chemicals present in landfill solid waste leach into water (precipitation run-off or groundwater) forming a pollutant landfill leachate stream. This stream is treated in wastewater treatment plants, emitting VOCs during aeration. Table 1 shows a summary of leachate composition from landfill sites (1).

TABLE 1: COMPOSITION OF LANDFILL LEACHATES - VOLATILE ORGANICS

Compounds	Concentration ( $\mu\text{g/L}$ ) Range
Benzene and alkylated benzenes	1100-2600
Toluene	4400-12300
Acetone	14000-32000
Higher Ketones (methyl ethyl, methyl isobutyl and methyl butyl)	11000-27000
Chloroethylenes (di-, tri- and tetra-)	1300-4300
Chloroform	1000-3100
Methylene chloride	8000-22000
Chloroalkanes	10-3850
Chlorobenzene	190-770

The conventional treatment methods for these gaseous pollutants are adsorption on a solid, absorption in a solvent, incineration or catalytic conversion. An alternative to these conventional treatment methods is the biological destruction of the VOCs. This method has the advantages of pollution destruction (as compared to transfer to another medium) and lower operation and maintenance costs. The proposed treatment scheme for the VOCs in the landfill leachate stream is shown in Figure 1. The leachate stream is first fed to a stripper where the VOCs are stripped from the liquid. The liquid effluent from the stripper is sent to the wastewater treatment plant. The gases coming out of stripper are fed to a biofilter where the VOCs are biologically degraded. The contaminant free gas can be discharged to atmosphere or recycled to the stripper. The biofilter process is discussed in the next section.

## DESCRIPTION OF THE BIOFILTER

A biofilter consists of a packed column containing biologically active mass. The support material can be of the following four types: 1) nonbiodegradable inactive material, such as glass or sand, which has no significant adsorption potential for the organics; 2) biodegradable inactive material, such as peat, with low adsorption potential for the organics, but has organic matter; 3) nonbiodegradable active material, such as activated carbon, which has high adsorption potential for organics; and, 4) biodegradable active material, such as polymeric adsorbent, which has adsorption potential for the organics and has biodegradable organic groups.

The biologically active matter (biomass) can exist either as a uniform biofilm on the support medium, or as a biomass particle trapped in the void spaces between the support material. In the case of a biofilm, the biomass is attached to the support material with simultaneous diffusion and degradation of the organics. In the case of a biomass particle, the organics degrade as they diffuse through the active biomass.

There are several important differences between the biofilter concept and conventional treatment technologies. The most important differences are as follows:

1. Vertical stratification of the microorganisms, with different predominant organisms existing at various levels of the biofilter bed height. Through the process of natural selection, microorganisms of a certain type will dominate at a specific height which maximizes their growth due to the existence of optimum conditions, such as, concentration of organics, pH, temperature, humidity, etc.

2. No breakthrough of the organic(s) due to continuous degradation as compared to breakthrough in an activated carbon system when its capacity is reached. Initially, the concentration of the organic(s) in the support material will increase until a steady state is established, when the rate of transport of the organic(s) from the gas phase to the support material is balanced by the rate of biodegradation of the organic(s).

3. Higher rate of biodegradation than in activated sludge systems due to the existence of an immobilized biofilm, which can contain a significantly higher concentration of the microorganisms than found in conventional activated sludge. Since the rate of biodegradation is dependent on the concentration of the microorganisms, a significantly higher concentration in the biofilm will result in an increased rate of biodegradation.

4. Potential of using a variety of organisms, either under aerobic or anaerobic conditions. Mixed cultures that have been acclimated to specific organics can be used as easily as pure cultures, which are capable of degrading certain organics only.

Aerobic and anaerobic biofilters can be used sequentially to degrade a mixture of organics containing components that are recalcitrant under aerobic conditions.

5. Less potential for contamination of support material by nonbiodegradable organics or high molecular weight contaminants, which is likely in the case of completely mixed continuous systems, such as activated sludge plants or fluidized bed reactors, handling aqueous waste streams. For the biofilter, the organic contaminants that are introduced through the gas phase would not have a high molecular weight or be recalcitrant compounds that can accumulate in the support material.

The above mentioned differences make the biofilter concept unique when compared to conventional technologies for removing organics from gaseous streams. In the following section, the mechanism of biodegradation in the biofilter has been discussed both qualitatively and modeled quantitatively.

#### MECHANISM OF BIODEGRADATION AND MODEL DEVELOPMENT

The microbial degradation of substrate is assumed to take place through the following steps:

1. Diffusion of substrate through bulk gas phase to gas-liquid interface;
2. Dissolution of substrate in the liquid phase (formed by the nutrient solution);
3. Diffusion of substrate through the liquid film which covers the biofilm on support;
4. Simultaneous diffusion with biodegradation of the substrate in the biofilm; and
5. Adsorption of the substrate on the support not covered by the biofilm.

Each of the above steps can be quantified using transport theory and can be mathematically expressed using equations containing the design and operating parameters of the biofilter, properties of the organic(s), and biodegradation kinetics variables.

The model assumptions are as follows:

1. The support is homogeneous and has a flat geometry.
2. Biodegradation takes place in the biofilm only.
3. The gas-liquid and biofilm-support interfaces are at equilibrium.

4. Biodegradation is first order with respect to the substrate. This assumption is justified at low concentrations of the substrate.

The material balance for the substrate in the biofilm yields the following equation:

$$\frac{\partial C}{\partial t} - D_e \frac{\partial^2 C}{\partial z^2} - k_1 C \quad (1)$$

where,

C = concentration of the substrate in the biofilm,  
 $D_e$  = effective diffusivity of the substrate in the biofilm,  
 $k_1$  = first order biodegradation rate constant,  
z = dimension co-ordinate, and  
t = time.

The initial and boundary conditions are given by the following equations:

$$C=0, \quad t \leq 0, \quad \text{all } z \quad (2)$$

Boundary condition at liquid-biofilm interface:

$$D_e \frac{\partial C}{\partial z} = K_L (p_A/H - C_2) \quad (3)$$

Boundary condition at biofilm-support interface:

$$D_e \frac{\partial C}{\partial z} = \frac{1}{\rho_p} \frac{\partial}{\partial t} \left[ \int_0^L C dz \right] \quad (4)$$

where;

$K_L$  = overall gas-liquid mass transfer coefficient,  
H = Henry's constant for the substrate,  
 $p_A$  = partial pressure of the substrate in the bulk gas phase,  
 $C_2$  = concentration of the substrate at the liquid-biofilm interface,  
 $\rho_p$  = support density,  
C = substrate concentration in the support, and  
L = characteristic dimension of the support.

The first boundary condition (equation 3) represents the continuity of the substrate flux at the liquid-biofilm interface. The second boundary condition (equation 4) is a material balance for the substrate in the support. In addition to these equations, the

following equation can be written for biofilm growth:

$$X \frac{d}{dt} (d_B) = \int_L^{L+d_B} (yk_1 C - bX) dz \quad (5)$$

where;

y = bacterial yield,  
 b = bacterial decay coefficient,  
 X = biomass concentration, and  
 d<sub>B</sub> = biofilm thickness.

The first term in parentheses after the integral sign in equation 5 gives the biomass yield due to biodegradation of substrate and the second term describes the decay of the biomass.

At steady state the solution of equations 1-5 becomes simplified. Steady state in the biofilm implies that the concentration profiles of the substrates are independent of time. There is no net growth of the biofilm and the thickness of the biofilm attains a constant value. The biodegradation rate attains a final value that does not change with time. The rate of transport of the substrate through the biofilm equals the rate of biodegradation. This results in a constant, non-zero concentration of the substrate in the biofilm-support material. The following three equations describe the steady state solution:

$$d_B^* = \frac{r}{\phi} C_3^* ((\cosh(\phi d_B^*))^2 - 1) \quad (6)$$

$$C_2^* = C_3^* \cosh(\phi d_B^*) \quad (7)$$

and,

$$C_3^* = 1 - \frac{\phi}{\phi_L} \frac{C_2^* \cosh(\phi d_B^*) - C_3^*}{\sinh(\phi d_B^*)} \quad (8)$$

where,

$$r = \frac{yk_1 P_A / H}{bX} \quad (9)$$

$$\phi = L \sqrt{\frac{k_1}{D_e}} \quad (10)$$

and,

$$\phi_L = L \frac{K_L}{D_e} \quad (11)$$

$C_3$  is the concentration of the substrate at the biofilm-support interface. The dimensionless quantities are defined as follows:

$$d_B^* = \frac{d_B}{L} \quad (12)$$

$$C^* = \frac{C}{P_A/H} \quad (13)$$

Equations 6, 7 and 8 can be solved simultaneously to obtain the concentration profile of the substrate in the biofilm. The degradation rate can then be obtained from the following equation:

$$R_A = K_L \frac{P_A}{H} (1 - C_2^*) \quad (14)$$

Equation 14 yields the biodegradation rate for the substrate on a single particle. This rate is utilized in the sizing of the biofilter. The mass balance on a differential element of the biofilter yields the following equation:

$$-G dy_A = R_A a A dz \quad (15)$$

where;

G = gas flow rate,

A = biofilter cross sectional area, and

$y_A$  = mole fraction of the substrate in the gas.

Substituting from equations 13 and 14, the following equation is obtained for the height of the biofilter:

$$Z = \frac{H G}{K_L a A P_c} \int_{y_{A_0}}^{y_{A_1}} \frac{dy_A}{(1 - C_2^*) y_A} \quad (16)$$

The kinetic parameters of the model can be evaluated from the experimental data. These parameters can then be utilized in the sizing and design of biofilter for a given load of volatile organic compounds.

#### BACKGROUND

While biological treatment of aqueous waste streams has been an established practice, using biofilters for treatment of air or gaseous streams has not been extensively investigated. Pomeroy (2) and Carlson and Leiser (3) have presented a similar approach for the removal of the sewage related odors. The main mechanism for the removal of odorous compounds, for example, hydrogen sulfide, mercaptans, terpenes, amines, etc., was adsorption on support material. There was no clear evidence of biodegradation. Smith et al. (4) determined that soil beds are effective in removing sulfur containing gases and can serve as sinks for hydrocarbons.

Hartenstein (5) has presented a range of operating conditions for a biofilter. He found that an important operating parameter is the moisture content of the filter bed, which plays an important part in determining removal efficiency. Eitner (6) determined that the most active microbes in a biofilter are the heterotrophic and chemo-organotrophic groups. He also noted that Actinomyces spp. are able to exploit a wide variety of organics and are reported to kill pathogens under certain conditions.

The distribution of microbes in the biofilter has been described by Ottengraf and van den Oever (7), Eitner (6) and Kampbell (8). The population density of the microbes is highest at the gas entrance at the bottom of the biofilter, and these microbes preferentially metabolize the more readily degradable influent compounds. The less degradable compounds are assimilated in the upper portions of the biofilter.

Eitner (6) presented data which indicated that significant reduction of the hydrocarbon concentration was achieved in approximately one week, and maximum removal rates were attained within one month of the operation. Ottengraf and van den Oever (7) investigated the survivability of the microbial flora in biofilters which were not loaded and showed that biofilter operation can be suspended for 14 days with only minimal loss in activity.

Biofilters have been traditionally used for controlling odors. Eitner and Gethke (9) showed that odors were reduced by approximately 98% at sewage treatment facilities. Prokop and Bohn (10) reported 99.9% removal rates for odors from an animal rendering facility.

Hartenstein (5) provided data which showed the percent removal of several organics as shown in Table 2.

TABLE 2: PERCENT REMOVAL OF ORGANICS IN A BIOFILTER  
[DATA OF HARTENSTEIN (5)]

Compound	% Removal
Hydrogen sulfide	99
Dimethyldisulfide	91
Terpene	98
Organo-sulfur gases	95
Ethyl benzene	92
Tetrachloroethylene	86
Chlorobenzene	69

Kampbell (8) measured removal rates between 95% and 99% for propane, isobutane, n-butane and trichloroethylene. Ottengraf and van den Oever (7) also measured high removal rates for toluene, butanol, ethylacetate and butylacetate.

Don and Feenstra (11) presented data comparing several alternative technologies for treatment of waste hydrocarbon gas streams and showed that biofilter is the most cost effective treatment method.

A biofilter system, consisting of prefabricated concrete parts which form an aeration plate to give uniform air distribution and drainage ducts, termed BIKOVENT system, was developed by Drs. Hans Gethke and Detlef Eitner of Aachen, Germany. The BIKOVENT system has been extensively used in Germany and Austria for odor control and controlling volatile organic compounds (VOCs) in waste air streams. The technology was recently introduced to the U.S. by Biofiltration Inc., Gainesville, Florida.

This paper reports on the experimental study on the biodegradation of volatile organic compounds present in landfill leachates in aerobic and anaerobic biofilters. The most abundant compounds in the leachate streams were targeted for study. A stripping study was carried out on the selected compounds to confirm Henry's law constant values.

## EXPERIMENTAL STUDIES

### STRIPPING OF LEACHATES

The characterization of vapor-liquid equilibria for landfill leachates (with respect to the volatiles of interest) was necessary in order to estimate the emission of the volatiles from the pollutant stream. It is expected that the stripping of the

volatiles will be governed by Henry's law for each compound. The interaction between various compounds in the multicomponent mixture can be neglected since the leachate streams form a dilute solution. The aim of the stripping experiments is to obtain Henry's constants for the compounds present in leachates. This was important to ensure that leachate constituents were not complexing the organics and thereby reducing Henry's law constant. The theoretical basis for these experiments has been described by Mackay et al. (12).

The experimental set up is shown in Figure 2. The experiments consist of bubbling the stripping agent (nitrogen gas) at a fixed flow rate through a leachate solution containing the volatiles and monitoring the concentration of the volatiles in this solution. The experimental conditions and results for stripping of methylene chloride, trichloroethylene and chloroform are shown in Table 3. It can be seen that, within experimental errors, Henry's constant can be used to describe the behavior of volatile organic compounds in leachates in a stripping operation.

TABLE 3: HENRY'S CONSTANTS FOR STRIPPING OF LEACHATES

Compound	Henry's constant ( $\text{m}^3 \text{ atm/mol} \times 10^3$ )			
	Water	Leachate 1	Leachate 2	Leachate 3
Methylene Chloride	3.19	2.75	2.28	2.0
Trichloroethylene	11.7	14.0	14.9	12.5
Chloroform	3.39	5.3	4.2	4.34

Experimental Conditions:

Volume of liquid: 1000 ml  
 Nitrogen flow rate: 100 ml/min  
 Time of run: 90 min  
 leachates 1 and 2 were two different leachates from sites in Delaware and leachate 3 was from Cincinnati.

BIOFILTER OPERATION

The VOCs from the landfill leachate streams were treated in a bench scale biofilter. The following three chemicals (substrates) were targeted for this study at the concentration shown below:

Toluene: 520 ppm  
 Methylene Chloride: 180 ppm  
 Trichloroethylene: 25 ppm

These three compounds were present in large concentration in the landfill leachate and were found to be present predominantly in the gas phase during the stripping study. Hence, when a landfill

leachate is stripped with gas, as shown in Figure 1, these chemicals are expected to be present in the gas stream which will be treated in a biofilter. The compound concentrations were selected to obtain preliminary experimental data. Further experimentation will be conducted using various concentrations of these compounds. A schematic of the bench scale biofilter apparatus is shown in Figure 3. Both the aerobic and anaerobic modes of degradation were investigated independently of each other. The substrates were fed to the biofilter through the gas phase. The requisite composition of the substrates in the gas phase was achieved by making the synthetic gas mixtures in a cylinder and subsequent blending with air or nitrogen. This was done to ensure a uniform feed concentration to the biofilter. The biofilter was packed with the support material. Nutrient solution with constituents as specified in Table 4 or Table 5 was circulated counter to the gas through the bed. The inlet and outlet gas streams were analyzed for the above three chemicals.

The details of the biofilter dimensions and operating conditions (for both aerobic and anaerobic operations) are shown below:

Support medium: activated carbon  
Support dimension: 4 mm  
Biofilter diameter: 25 mm  
Packed height: 600 mm (jacketed)  
Gas flow rate: 150 ml/min  
Gas superficial velocity: 0.533 cm/s  
Liquid flow rate: 10 ml/min  
Liquid superficial velocity: 0.033 cm/s

The biofilters contained active acclimated biomass. The biomass acclimated to the above substrates was obtained in the following manner: Biomass from a pilot scale activated sludge plant treating hazardous waste was suspended in the bioreactor (column 100 mm dia., 700 mm height). The bioreactor was fed daily with the three substrates. Nutrients necessary for the growth were also added weekly. The aerobic bioreactor was aerated by air. The anaerobic bioreactor was operated similarly (but without any aeration) with seed biomass from the anaerobic digester. The biomass in the anaerobic bioreactor was kept suspended by operating a recirculation loop at a high flow rate.

The biomass from the bioreactor was transferred to the biofilter by circulating the bioreactor suspension through the biofilter. It was found that the biomass could be effectively transferred from the bioreactor to the biofilter.

Specific details on the aerobic and anaerobic biofilters have been discussed in the next two sections.

### Aerobic Biofilter

The synthetic gas mixtures of the substrates were prepared in air for aerobic operations. The composition of the aerobic nutrient

solution is given in Table 4.

The inlet and outlet gas and liquid streams were analyzed for the volatile organic compounds mentioned above using a gas chromatograph (EPA standard method 602).

TABLE 4: COMPOSITION OF NUTRIENT SOLUTION FOR AEROBIC BIOFILTER

Salt	Concentration (mg/L)
$\text{KH}_2\text{PO}_4$	85.0
$\text{K}_2\text{HPO}_4$	217.5
$\text{Na}_2\text{HPO}_4$	266.4
$\text{NH}_4\text{Cl}$	25.0
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	22.5
$\text{CaCl}_2$	27.5
$\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$	0.25
Trace Elements-	
$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$	0.0399
$\text{H}_3\text{BO}_3$	0.0572
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.0428
$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$	0.0347
$\text{FeCl}_3 \cdot \text{EDTA}$	0.10
Yeast Extract	0.15

### Anaerobic Biofilter

For anaerobic operation, the synthetic mixture of the compounds was prepared in nitrogen. Nitrogen was scrubbed in a solution of sodium thiosulfite (with resazurin as an indicator) to remove the traces of oxygen prior to being fed to the biofilter. The biofilter was maintained at constant temperature (35 °C.) by circulating hot water through the biofilter jacket. The composition of the anaerobic nutrient solution is shown in Table 5.

The inlet and outlet concentrations of the compounds in the gas and liquid streams were monitored using a gas chromatograph (EPA standard method 602).

TABLE 5: COMPOSITION OF NUTRIENT SOLUTION FOR ANAEROBIC BIOFILTER

Salt	Concentration (mg/L)
Ammonium Chloride	1200
Magnesium Chloride	500
Potassium Chloride	400
Calcium Chloride	25
Ammonium Phosphate	80
Ferrous Chloride	40
Cobalt Chloride	2.5
Potassium Iodide	2.5
Manganese Chloride	0.5
Ammonium Vanadate	0.5
Zinc Chloride	0.5
Sodium Molybdate	0.5
Boric Acid	0.5
Nickel Chloride	0.5
Cysteine	10
Sodium Bicarbonate	6000

## RESULTS AND DISCUSSION

It was found that the amount of compound removed from the gas phase that can be accounted for by the increase in the liquid phase concentration of the compound was negligible for both aerobic and anaerobic operations. This means that the compound removed in the biofilter by the trickling nutrient flow was negligible as compared to the feed rate of the compound. Removal efficiency of the biofilter for a compound was defined as the amount of compound removed from the gas phase expressed as a percentage of the amount of that compound fed to the biofilter through the gas phase. The removal efficiency can be calculated simply by taking the ratio of difference in the inlet and outlet concentrations of the compound in the gas phase to the concentration of the compound at the inlet. The steady state removal efficiencies of both the aerobic and anaerobic biofilters for the three compounds are shown below in Table 6.

TABLE 6: REMOVAL EFFICIENCIES OF THE BIOFILTER

Compound	Removal Efficiency, %	
	Aerobic Biofilter	Anaerobic Biofilter (unsteady state)
Toluene	80	60
Methylene Chloride	25	20
Trichloroethylene	40	40

It should be noted that these removal efficiencies are a function of the nutrient concentration. Since the impact of the nutrients on removal efficiency has not been fully studied, numbers given in Table 6 are preliminary and subject to modification pending further research. The average biodegradation rates obtained in the biofilter for each of the compounds are shown in Table 7.

TABLE 7: AVERAGE BIODEGRADATION RATES

Compound	Average Biodegradation Rate, mg substrate/cm <sup>3</sup> biofilter min	
	Aerobic Biofilter	Anaerobic Biofilter (unsteady state)
Toluene	$8.7 \times 10^{-4}$	$6.5 \times 10^{-4}$
Methylene Chloride	$8.7 \times 10^{-5}$	$6.96 \times 10^{-5}$
Trichloroethylene	$3.0 \times 10^{-5}$	$3.0 \times 10^{-5}$

It can be seen that the removal efficiency of the biofilters for any of the compounds is less than 100%. However, efficiencies approaching total removal of substrates can be obtained by providing more residence time for the gas or increasing nutrient concentration. This can be achieved by decreasing the gas flow rate for the biofilter, or alternately, by increasing the height of the biofilter.

It can also be seen that the removal efficiencies of the aerobic and anaerobic biofilters differ for the three compounds. Differing intrinsic kinetics of biodegradation and other factors such as diffusional resistances and biomass concentration result in different aerobic and anaerobic biofilter heights for a given degree of removal for the substrate.

It was also found that trichloroethylene could be degraded under aerobic conditions in the presence of a co-metabolite such as toluene.

## CONCLUSIONS

1. The volatile organic compounds present in the leachate streams can be stripped according to Henry's constant for these compounds in water. This shows that leachate constituents do not change Henry's law constant significantly.

2. The compounds can be removed from gas stream by aerobic as well as anaerobic degradation in a biofilter.

## ACKNOWLEDGEMENT

We are thankful to Professor M. Suidan, Civil and Environmental Engineering, University of Cincinnati, and Mr. S. I. Safferman and Mr. R.C. Brenner, U.S. EPA for their help in carrying out this research.

## NOMENCLATURE

A	Cross sectional area of the biofilter, $\text{cm}^2$
b	Bacterial decay, $\text{sec}^{-1}$
C	Substrate concentration in the biofilm, $\text{mol}/\text{cm}^3$
$\bar{C}$	Substrate concentration in the support, mol substrate/gm support
$C_2$	Substrate concentration at the liquid-biofilm interface, $\text{mol}/\text{cm}^3$
$C_3$	Substrate concentration at the biofilm-support interface, $\text{mol}/\text{cm}^3$
$d_B$	Biofilm thickness, cm
$D_e$	Effective diffusivity of the substrate in the biofilm, $\text{cm}^2/\text{sec}$
G	Gas flow rate, mol/sec
H	Henry's constant, $\text{atm m}^3/\text{mol}$
$k_1$	First order biodegradation rate constant, $\text{sec}^{-1}$
$k_L$	Overall gas-liquid mass transfer coefficient, $\text{cm}/\text{sec}$
$K_{La}$	Overall volumetric gas-liquid mass transfer coefficient, $\text{sec}^{-1}$
L	Characteristic dimension of the support, cm
$p_t$	Total gas pressure, atm
$p_A$	Partial pressure of substrate A, atm
r	Biomass growth/decay ratio, dimensionless
$R_A$	Biodegradation rate of A, $\text{mol}/\text{cm}^2 \text{ sec}$
$R_{Aa}$	Volumetric degradation rate of A, $\text{mol}/\text{cm}^3 \text{ sec}$
t	Time, sec
X	Biomass concentration, $\text{gm}/\text{cm}^3$
Y	Bacterial yield, gm biomass/ mol substrate
$y_A$	Mol fraction of A in gas, dimensionless
z	Dimension co-ordinate, cm
Z	Height of the biofilter, cm
$\phi$	Kinetic parameter, dimensionless
$\phi_L$	Mass transfer parameter, dimensionless
$\rho_p$	Support density, $\text{gm}/\text{cm}^3$

superscript

\* Dimensionless quantity

subscripts

i At the inlet of the biofilter

o At the outlet of the biofilter

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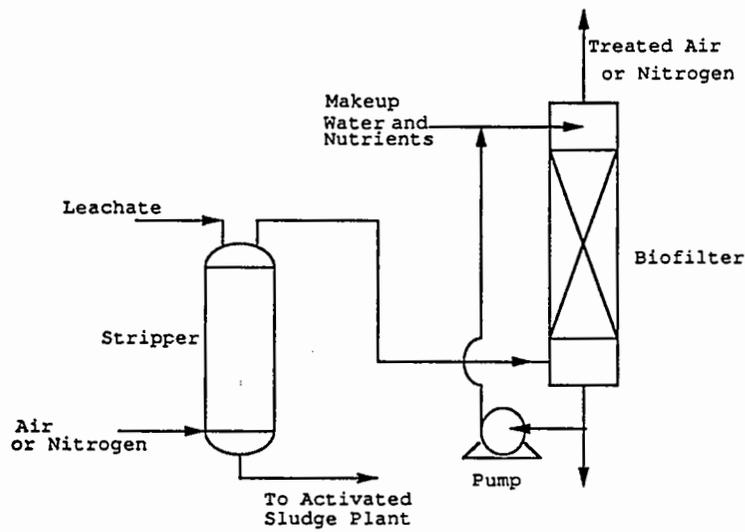


Figure 1: Schematic of the Biofilter Treatment Scheme

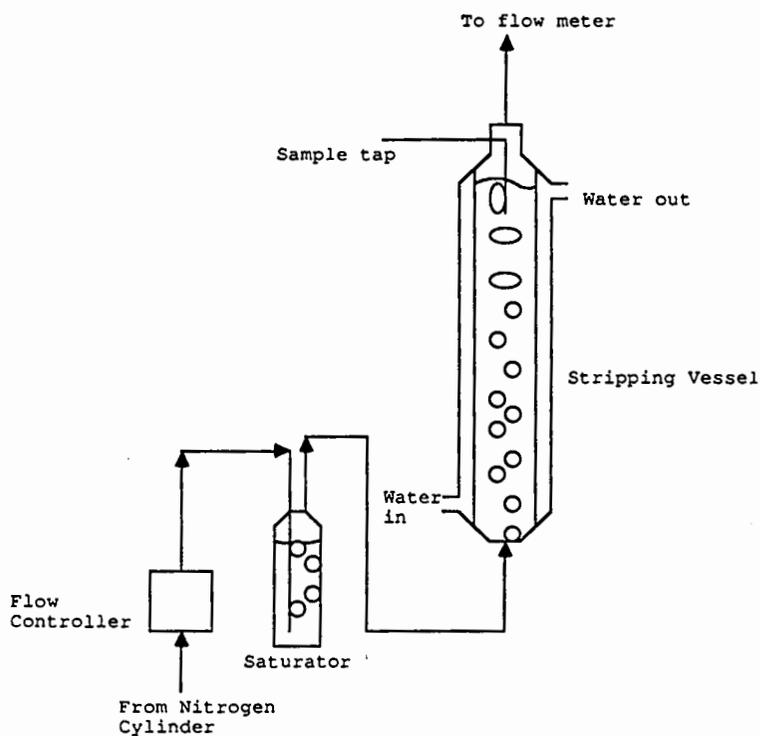


Figure 2: Experimental Set up for Stripping

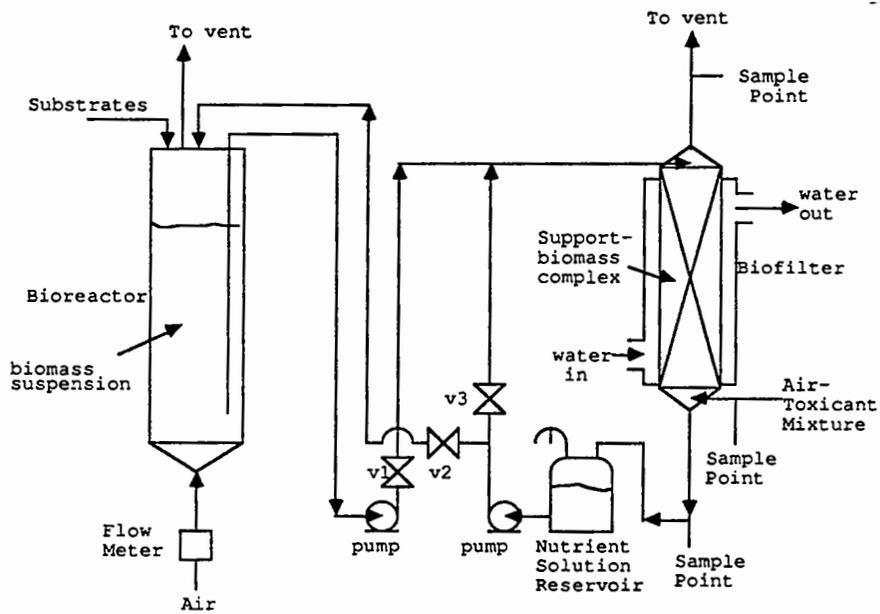


Figure 3: Schematic of Bioreactor-Biofilter System

SCREENING OF COMMERCIAL BIOPRODUCTS FOR ENHANCEMENT OF  
OIL BIODEGRADATION IN CLOSED MICROCOSMS

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ABSTRACT

Ten commercial products designed to enhance oil biodegradation were tested in the laboratory. The products were used according to manufacturers' directions. The performance of each product was assessed by measuring: onset, rate, and extent of O<sub>2</sub> uptake in a respirometer; disappearance of oil components by GC and GC/MS; and growth of microorganisms on crude oil agar and marine agar. Products selected for field testing were required to outperform ordinary mineral nutrients in enhancing oil biodegradation. Two products, E and G, were found to outperform mineral nutrients in O<sub>2</sub> uptake and removal of oil components. Both E and G produced rapid O<sub>2</sub> uptake and a greater net O<sub>2</sub> uptake than mineral nutrients alone. Similarly, alkane and aromatic hydrocarbon reduction was more extensive than mineral nutrients alone. The other products either matched performance with mineral nutrients or were much poorer in the choice criteria.

## INTRODUCTION

Bacterial degradation of petroleum hydrocarbons has been known and recognized for decades. The subject has been reviewed comprehensively in the literature (1,2,4), the most recent one appearing this year (5). Vestal et al. (6) reported that, although oil degraders comprise approximately 1% of the total heterotrophic population in unpolluted waters, the oil degrader population increases to as high as 10% in response to a spill. In 1989, research conducted by the U.S. Environmental Protection Agency (EPA) in Prince William Sound demonstrated that microbial communities on the contaminated beaches were highly competent in their ability to degrade the Prudhoe Bay crude that was spilled from the Exxon Valdez (7). The purpose of the latter study was to determine if application of water soluble and oleophilic nutrients could enhance the natural biodegradation rate.

After the EPA study showed that bioremediation of oil-polluted beaches was enhanced by the addition of fertilizer, the question then arose whether further enhancement was possible with the addition of microbial inocula prepared from oil degrading populations not indigenous to Alaska. Seeding experiments have been done in previous studies with mixed results (5). In a recent study, Dott et al. (8) compared nine commercial mixed bacterial cultures to activated sludge microorganisms for their ability to degrade fuel oil in laboratory flasks. They found that fuel oil degradation by the naturally occurring bacteria in activated sludge did not depend on, nor was it enhanced by the application of highly adapted commercially available cultures. Most success has been achieved when chemostats or fermenters are used to control conditions or reduce competition from indigenous microflora (9).

In February, 1990, the U.S. Environmental Protection Agency issued a public solicitation for proposals to the bioremediation industry on testing the efficacy of commercial microbial products for enhancing degradation of weathered Alaskan crude oil. The Agency commissioned the National Environmental Technology Applications Corporation (NETAC), a non-profit corporation dedicated to the commercialization of environmental technologies, to convene a panel of experts to review the proposals and choose those that offered the most promise for success in the field. Forty proposals were submitted, and 11 were selected for the first phase of a two-tiered testing protocol (only 10 were tested because one company did not participate). The laboratory testing consisted of electrolytic respirometers set up to measure oxygen uptake over time and shake flasks to measure oil degradation and microbial growth. If one or more products were found effective, the second tier would take place, consisting of small field plots on an actual contaminated beach in Prince William Sound in the summer of 1990. This paper discusses the first phase of testing, the laboratory batch flask and respirometric evaluations.

The objective of the laboratory protocol was to determine if commercial bioremediation products can enhance the biodegradation of weathered crude oil to a degree significantly better than that achievable by simple fertilizer application. Testing was conducted in a controlled and closed environment designed to give quick results under ideal conditions. It was not meant to

simulate the open environment of the oiled beaches of Prince William Sound, where conditions are in a constant state of flux with respect to tidal cycles and washout, temperature variation, climatic changes, freshwater/saltwater interactions, etc. The organisms inside the respirometer vessels were in continuous contact with the oil, seawater, and nutrients added initially, and the seawater was not replenished every 12 hours as is the case in nature. The test was merely a screening procedure that was designed to determine if there was sufficient enhancement due to the commercial additives that would justify proceeding to the next tier of testing. To proceed to the field phase, three lines of evidence were used for decision-making: rapid onset and high rate of oxygen uptake, substantial growth of oil degraders, and significant degradation of the aliphatic and aromatic fractions of the weathered Prudhoe Bay crude oil.

The 10 companies participating in the laboratory testing phase were (in alphabetical order): Alpha Environmental, Bioversal, Elf Aquitaine, ERI-Microbe Masters, Imbach, Microlife Technics, Polybac, Sybron, Waste Microbes, and Woodward Clyde. Specific products and companies cannot be identified to preserve confidentiality.

## MATERIALS AND METHODS

### ELECTROLYTIC RESPIROMETRY

The studies were conducted using four automated continuous oxygen-uptake measuring Voith Sapromats (Model B-12). The instrument consists of a temperature-controlled water bath containing measuring units; a recorder for digital indication and direct plotting of the oxygen uptake velocity curves; and a cooling unit for the conditioning and continuous recirculation of water bath volume. The recorder displays a digital readout of oxygen uptake and constructs a graph of the data for each measuring unit. The cooling unit constantly recirculates water to maintain a uniform temperature in the water bath. The measuring units are comprised of 12 reaction vessels each with a carbon dioxide absorber mounted inside, 12 oxygen generators each connected to its own reaction vessel by tubing, and 12 pressure indicators connected electronically to the reaction vessels. The measuring units are interconnected by tubing, forming an air-sealed system, so that the atmospheric pressure fluctuations do not adversely affect the results.

Depletion of oxygen by microbiological activity creates a vacuum, which is sensed by the pressure indicator. The oxygen generator is triggered to produce just enough oxygen to counterbalance the negative pressure. The current used to generate the oxygen is measured by the digital recorder, and the data are converted directly into mg/L oxygen uptake. The CO<sub>2</sub> produced by microbial activity is absorbed by soda lime. The nitrogen/oxygen ratio in the gas phase above the sample is maintained throughout the experiment, and there is no depletion of oxygen. The oxygen generators of the individual measuring units are electrolytic cells that supply the required amount of oxygen by electrolytic decomposition of copper sulfate/sulfuric acid solution.

A recorder/plotter constructs an oxygen uptake graph as a function of time and displays it on the computer screen while digitally saving the data on disc. For frequent recording and storage of oxygen uptake data, the Sapromat B-12 recorders are interfaced to an IBM-AT personal computer via the Metrobyte interface system. A software package allows the collection of data at 15 minute intervals.

#### EXPERIMENTAL DESIGN

All commercial products were tested in duplicate at the concentration recommended by the manufacturer. Each experimental respirometer flask was charged with the following materials in the order listed: weathered crude oil, 250 mg; 250 mL seawater from Prince William Sound; and commercial product at the concentration specified by the manufacturer. Seawater was prepared as follows: 25 g of oiled rocks from a contaminated beach in Prince William Sound was placed in a 4-L flask to which was added 2 L of seawater. The mixture was shaken for approximately 30 minutes to wash off a microbial inoculum from the rocks. The flask contents were allowed to settle, and 10mL of supernatant was mixed in each respirometer vessel. The following table presents the summarized experimental design showing all control and experimental flasks.

TABLE 1. EXPERIMENTAL DESIGN FOR RESPIROMETRIC STUDIES.

Reaction Vessel	Weathered Oil	Commercial Product	Seawater	TOTAL
<u>TEST FLASKS:</u>				
TPn	+	+	+	20
F1,2	+	-	+	2
<u>CONTROL FLASKS:</u>				
CPn	-	+	+	20
CF1,2	-	-	+	2
C1-inoculum	-	-	+	2
C2-no nutrients	+	-	+	2
TOTAL				48

TPn = duplicate commercial product flasks (n = 10)  
 F1,2 = fertilizer flasks (mineral N and P nutrients)  
 CPn, CF1,2 = no-oil controls for products and fertilizer, respectively  
 C1, C2 = inoculum and no-nutrient controls

Flasks F1 and F2 represented simple inorganic fertilizer application and contained the following ingredients (mg/L final concentration):  $\text{KH}_2\text{PO}_4$ , 6.33;  $\text{K}_2\text{HPO}_4$ , 16.19;  $\text{Na}_2\text{HPO}_4$ , 24.86;  $\text{NH}_4\text{Cl}$ , 38.5;  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 45;  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 55;  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 2.5. The following additional trace elements were included in the formulation ( $\mu\text{g/L}$  final concentration):  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , 60.4;  $\text{H}_3\text{BO}_3$ , 114.4;  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , 85.6; and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , 69.4.

All respirometer flasks were incubated at  $15^\circ\text{C}$  in the dark and continuously stirred at 300 rpm by magnetic stirrers. The first set of control flasks (CPn, CF1,2) represented background oxygen uptake of the product and seawater without oil. Results from these flasks were subtracted from the appropriate test flasks to obtain the net oxygen uptake on the weathered oil. The inoculum control represented the endogenous oxygen uptake of the organisms from the washed beach material and the seawater alone. The no-nutrient control represented the oxygen uptake of the organisms from the washed beach material and seawater on weathered oil without any external source of nutrient addition (i.e., background nutrient levels from Prince William Sound).

## FLASK EXPERIMENTS

Shaker flasks duplicating the respirometer flasks were used to assess the quantitative changes in oil composition by chromatographic separation of the individual components. Although it was possible to remove samples from the respirometer flasks, it was deemed more prudent not to disturb the respirometric runs but instead have the shake flasks with proportionately higher levels of oil, commercial products, etc., to facilitate sampling for and precision/accuracy of the analytical chemistry. Table 2 summarizes the shaker flask experimental design.

The test flasks corresponded exactly to the 22 test flasks listed in Table 1 but with the following modifications: flask size, 250 mL; seawater, 100 mL; weathered oil and commercial products, 10 times the final concentrations used in the respirometer flasks; and mineral nutrients, same final concentration used in the respirometer flasks. The higher concentration of weathered oil was used to improve the final sensitivity of the chemical analyses.

In addition to the 22 test flasks, 18 supplemental flasks were set up. These reactors represented 9 sterile product controls, which determined whether the enhancement was due to the microorganisms or to the nutrients or metabolites in the product, and 9 sterile background controls (i.e., sterile oil and seawater, but non-sterile product) to evaluate the effect of competition from naturally occurring organisms (one of the 10 products did not receive these sterile treatments). Sterilization of materials was accomplished by autoclaving at  $121^\circ\text{C}$  for 15 minutes.

## SAMPLING

There were three sampling events for analytical chemistry and microbiology: day 0, day 11, and day 20. These events were determined by the

shape of the oxygen uptake curves from the respirometry experiments. Each shaker flask was sacrificed at the indicated sampling time by mixing the contents with methylene chloride and performing the extraction on the entire mixture. Before sacrificing a flask, a small aliquot was removed for determination of microbial density changes.

TABLE 2. EXPERIMENTAL DESIGN FOR THE SHAKER FLASK STUDIES.

Reaction Vessel	Weathered Oil	Commercial Product	Seawater	TOTAL
<u>TEST FLASKS:</u>				
TPn	+	+	+	20a
SPn	+	sterile	+	9a
TPnSb	sterile	+	sterile	9a
F1,2	+	-	+	2a
<u>CONTROL FLASKS:</u>				
CPn	-	+	+	10b
CF1	-	-	+	1b
C1-inoculum	-	-	+	1b
C2-no nutrients	+	-	+	2a
TOTAL				54

TPn = duplicate commercial products (n = 10), non-sterile system  
 SPn = sterile products in non-sterile seawater/oil, non-duplicated  
 TPnSb = non-sterile products in sterile seawater/oil, non-duplicated  
 F1,2 = fertilizer (mineral N and P nutrients) in non-sterile system  
 CPn, CF1 = no-oil controls for products and fertilizer, respectively  
 C1, C2 = inoculum and no-nutrient controls  
 a = microbiological and chemical analysis  
 b = microbiological analysis only

## ANALYTICAL CHEMISTRY

The oil constituents were analyzed by measuring the aliphatic and aromatic fractions of the methylene chloride extracts. The extracts were concentrated and passed through a silica gel fractionation column to separate the alkanes and the aromatics. The column was first eluted with hexane to collect the alkane fraction and then a 1:1 mixture of hexane and benzene to collect the aromatic fraction. Any polar compounds remaining in the extract stayed bound to the silica gel column. Aliphatic fractions were measured by gas chromatography using a flame ionization detector. The aromatic fractions were characterized by gas chromatography/mass spectrometry (GS/MS).

## NUTRIENT ANALYSIS

The nitrogen species NH<sub>3</sub>-N, NO<sub>2</sub>--N, and NO<sub>3</sub>--N were determined by U.S. EPA Methods (10). The NH<sub>3</sub>-N method was No. 350.1 and the NO<sub>2</sub>-N/NO<sub>3</sub>-N method was No. 353.1.

## MICROBIOLOGICAL TESTING

Growth of oil degraders was measured by spread plates on oil agar (Bushnell-Haas medium supplemented with Prudhoe Bay crude oil as the carbon source) (3). Total heterotrophic bacterial numbers were estimated by spread plate culture on Marine Agar 2216 (Difco). Plates were incubated at 15°C for 21 days prior to counting.

## RESULTS

Nutrient Levels in Each Product. Product flasks requiring nutrient addition, as specified by the product manufacturer, received the same level of mineral nutrients as the fertilizer flasks. The ammonia-nitrogen concentrations measured in each product flask at day 0 are summarized in Table 3.

TABLE 3. NH<sub>3</sub>-N LEVELS IN EACH PRODUCT FLASK AT THE START OF THE EXPERIMENT.

PRODUCT	NH <sub>3</sub> -N mg/L	NUTRIENTS ADDED
A	8.0	YES
B	2.1	NO
C	1080.0	NO
D	11.8	YES
E	11.3	YES
F	10.0	YES
G	24.9	YES
H	426.0	NO
I	0.5	NO
J	1.5	NO
FR*	6.9	YES

\*FR = mineral fertilizer

## STATISTICAL ANALYSIS OF ALKANE DEGRADATION DATA

The percent reductions of the resolved aliphatic constituents of the weathered oil (n-C12 through n-C34 plus the branched-chain compounds pristane and phytane) were computed at day 11 for each product flask and the results compared to the percent reduction computed for the mineral nutrient flasks. Table 4 summarizes the statistical differences observed using Tukey's Studentized Range Test (11). The products are arranged in descending order of significance. Only Products E and G gave significantly higher removals ( $p < 0.05$ ) than inorganic fertilizer after 11 days. Six of the other products gave results no different from mineral nutrients, while two actually gave significantly lower removals. The latter results suggest that the products may have been toxic to the biomass at the levels used in the closed flasks.

TABLE 4. TUKEY'S STUDENTIZED RANGE TEST FOR DETECTING DIFFERENCES IN MEAN PERCENT REMOVAL OF ALKANES BY PRODUCTS IN 11 DAYS

PRODUCT	% REMOVAL	SIGNIFICANTLY DIFFERENT FROM INORGANIC NUTRIENTS*
E	94.5	YES
G	93.6	YES
B	87.9	NO
A	75.9	NO
D	74.2	NO
FR	68.4	NO
C	67.8	NO
J	59.9	NO
H	49.5	NO
F	33.3	YES
I	27.9	YES

\*Minimum Detection Difference = 21.3% at 5% Significance Level

### TOTAL ALKANE REDUCTION

The total alkane degradation data from the product flasks and the corresponding sterile controls at days 11 and 20 are summarized in Figure 1.

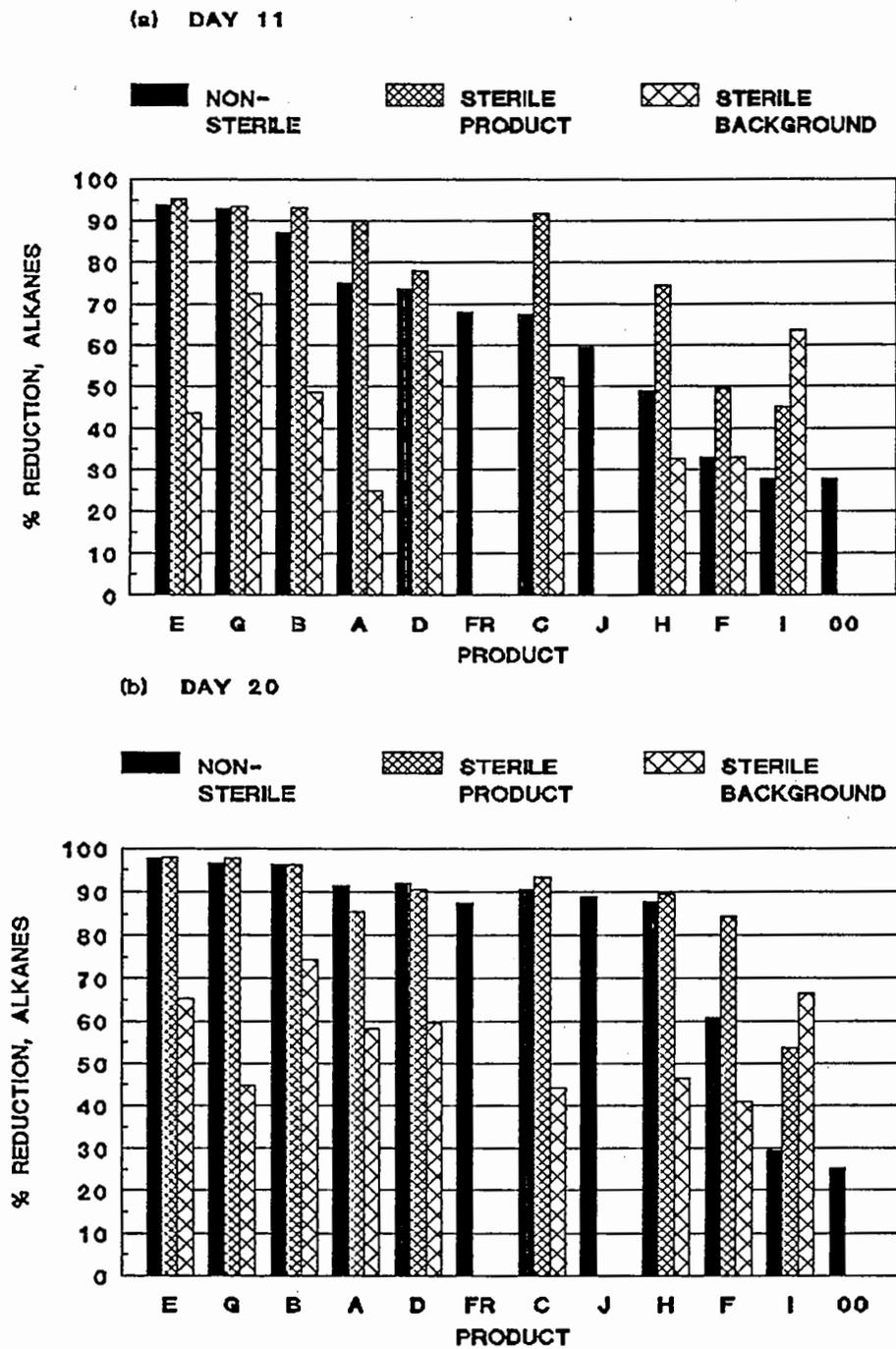


Figure 1. Total alkane reduction in the product flasks. (a) day 11, (b) day 20.

The products are arranged on the x-axis in the order determined by the statistical analysis (this same ordering has been made on all figures). At day 11 (top half of Figure 1), better degradation was observed in every case when the commercial products were first sterilized, suggesting that the indigenous Alaskan populations were doing most if not all of the bioremediation. In contrast, less degradation occurred in every case except Product I when the background (seawater and oil) was first sterilized. This suggests that, when left alone, the product organisms were less able to degrade the alkane fraction than the indigenous organisms. In the non-sterile treatments, enhancement was observed for Products E and G compared to mineral nutrients, suggesting that the products exhibiting the enhancement were providing metabolites or some other form of nutritional benefit that was lacking in the mineral nutrient flask. By day 20 (bottom half of Figure 1), all products except Products F and I caught up, giving greater than 85% reduction in the total alkane levels in the flasks. However, most of the flasks containing oil and seawater that were first sterilized still significantly lagged behind the non-sterile systems.

#### TOTAL AROMATICS REDUCTION

A summary of the total aromatics reduction data at day 11 and 20 is presented in Figure 2. Differences are less clear among the products, although Products C, F, H, and I gave total reductions considerably less than mineral nutrients. By day 20, aromatic reduction by Product C was somewhat closer to the others, while Products H, F, and I substantially lagged. Excellent removal of aromatics was observed in all other flasks.

#### RESPIROMETRIC RESULTS

The net oxygen uptake curves (oxygen uptake in product flasks with oil minus oxygen uptake in flasks without oil) for all 10 products (curves with symbols) compared to mineral nutrients (curve with no symbols) are summarized in Figure 3a and 3b. In Figure 3a the two products giving significantly higher alkane degradation, E and G, also exhibited higher net oxygen consumption than mineral nutrients. The final plateau in total oxygen uptake was slightly less than 500 mg/L for both Products E and G compared to about 340 mg/L for the mineral nutrient flasks. The acclimation lag period for products E and G were approximately 2 and 4 days, respectively, compared to 5 days with mineral nutrients. Product A gave the highest maximum net uptake (630 mg/L compared to 340 for mineral nutrients) but the lag period was almost 10 days. Products B and D exhibited O<sub>2</sub> uptake characteristics no different from the nutrient control.

In Figure 3b only products J and C gave higher overall net O<sub>2</sub> consumption than mineral nutrients, although product F exceeded the control after 27 days. The lag period for both products J and C was only 1 day. The shape of the product F curve was multi-phasic, suggesting the organisms were consuming different substrates at different rates and at different times (diauxie). Very little net oxygen consumption was observed with product I.

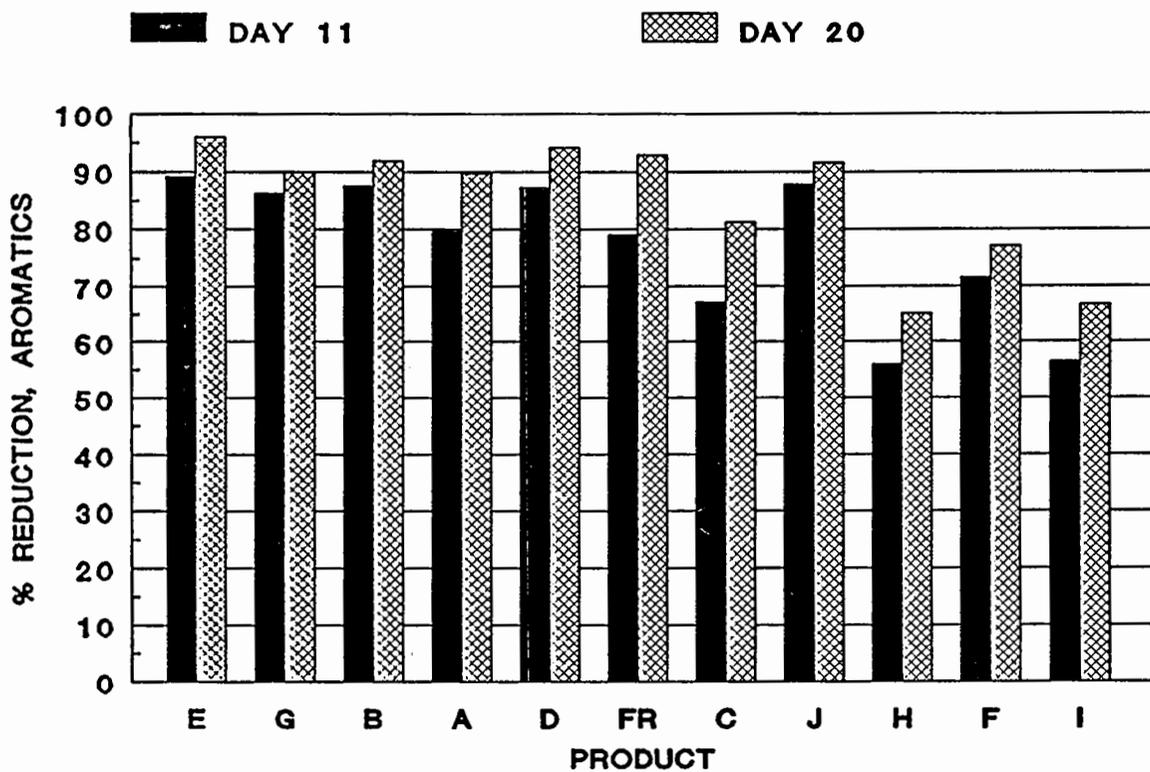
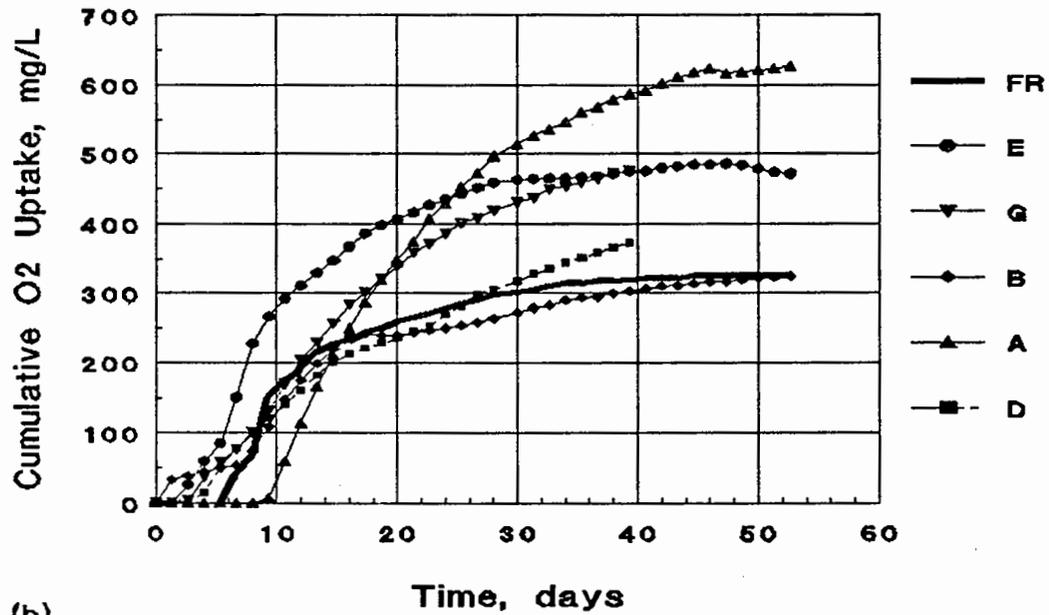


Figure 2. Total aromatics reduction in the product flasks at days 11 and 20.

(a)



(b)

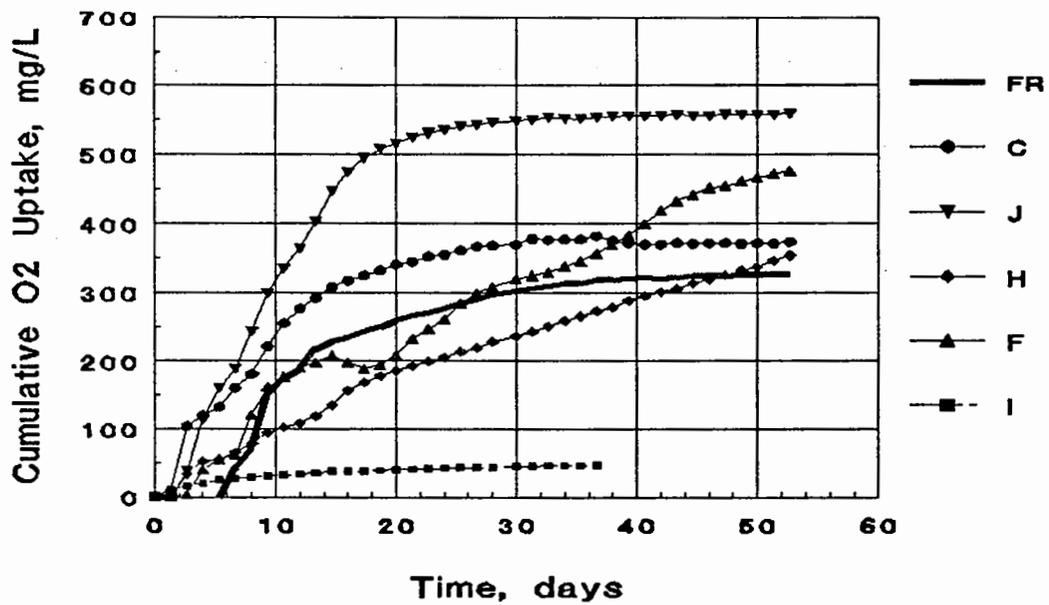


Figure 3. Net oxygen uptake curves for products and mineral nutrients: (a) products E,G,B,A,D (b) products C,J,H,F,I.

## MICROBIOLOGICAL RESULTS

Virtually all changes in oil degrader densities occurred by day 11. The populations levelled off in all flasks thereafter. Consequently, the growth of oil degraders has been summarized for days 0 and 11 only, and the results are presented in Figure 4.

Products E and G, which gave the best alkane degradation of all the products (Table 4 and Figure 1) and displayed net oxygen uptake characteristics superior to most (Figure 3a), also exhibited excellent growth of oil degraders in 11 days. Products C, J, and F yielded high levels of oil degraders and good oxygen uptake curves, but alkane degradation was no better than the populations growing in simple mineral nutrients. Oil degrader populations actually declined in the product B flasks, and the increase in oil degraders in the flasks containing products A, D, and I was minimal.

## DISCUSSION

The objective was to determine whether a commercial bioremediation product was able to effect weathered crude oil degradation better than natural Prince William Sound organisms when stimulated with simple mineral nutrients. Oil degradation chemistry, oxygen uptake in respirometer flasks, and microbial density changes were used to decide which product(s) would proceed to field testing.

Of all the products tested, the two that provided the most consistent results in all three tests were products E and G. Both gave higher oxygen uptake, greater growth in oil degraders, and superior alkane degradation than mineral nutrients. Two of the products, C and J, showed good growth of oil degrader populations and gave excellent net oxygen uptake curves but were no better than indigenous populations stimulated with simple mineral nutrients. Product F yielded the highest oil degrading population of all, yet its oxygen uptake curve was no better than the mineral nutrient curve until after day 27, and alkane degradation was relatively poor. Product A gave the best overall net oxygen consumption, but the increase in oil degraders and the relative alkane degradative capability were mediocre, as were the flasks containing products B, D, H, and I.

The sterile controls revealed that the indigenous Alaskan oil-degrading populations were performing most if not all of the biodegradative activity. The organisms present in products E and G did not appear to contribute significantly to such activity. This suggests that a co-metabolite or a nutrient or some other unknown factor exists in these two products that stimulates the indigenous microorganisms to degrade the crude oil constituents at rates faster than is possible with simple nutrient addition. Further work needs to be done to define the enhancement factor in these products.

Correlations have not as yet been made between weathered crude oil degradation and oxygen uptake, nor have carbon balances been performed. Work is being planned to measure carbonaceous metabolic end products, CO<sub>2</sub> production, and total biomass yield, and then to correlate this information

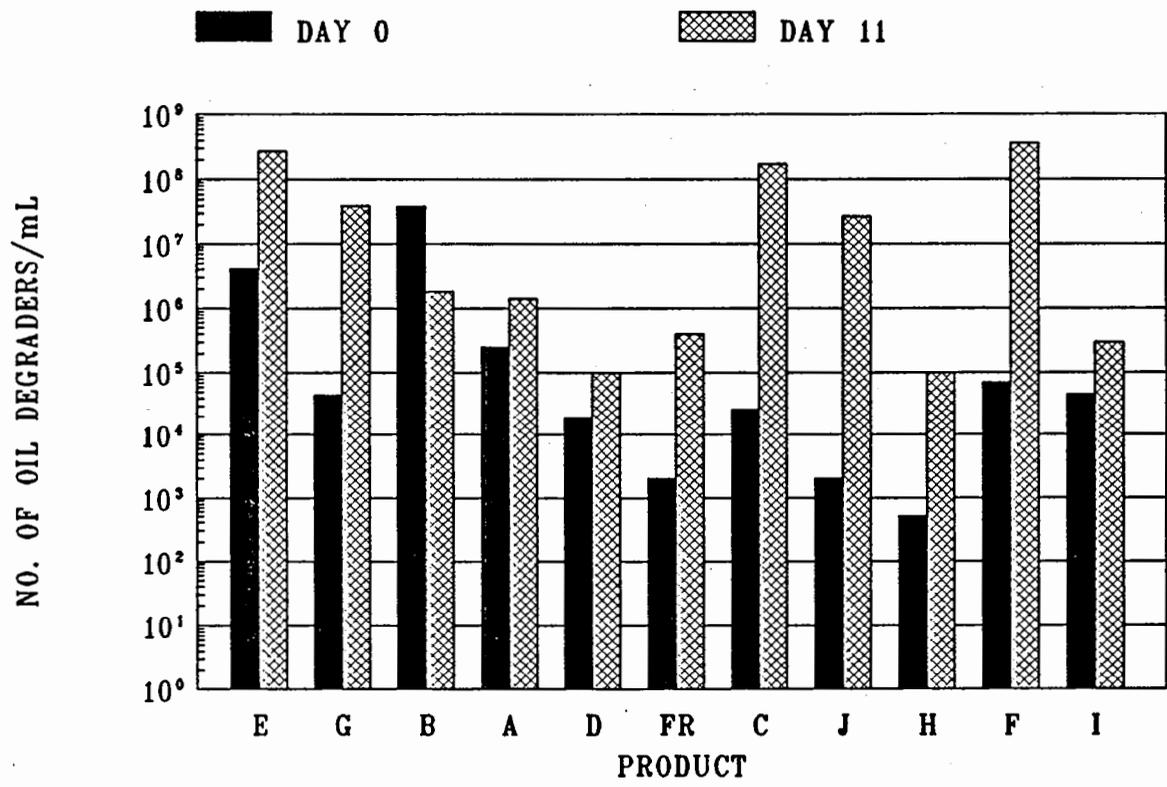


Figure 4. Growth of oil degraders in the product flasks.

with the oxygen consumption data. If such correlations can be established, then use of oxygen consumption data for estimating biodegradation efficacy as part of a screening protocol will be made possible. The respirometric technique requires much less effort than conventional shake flask studies because data gathering is automated and computerized, and it is not necessary to collect samples manually during the course of a biodegradation experiment. All that is required, assuming the proper correlations have been established, is the careful measurement of initial substrate and biomass values followed by the measurement of the residual soluble product value at the plateau of the uptake curve (12). From the analysis of this information, treatment decisions can be facilitated.

#### CONCLUSIONS

Results from all three lines of evidence, i.e., respirometry, microbiology, and oil chemistry, supported the decision to field test only products E and G. It appears from all the available evidence that the indigenous Alaskan microorganisms were primarily responsible for the biodegradation in the closed flasks and respirometer vessels, and that any enhancement provided by products E and G might have been due simply to metabolites, nutrients, or co-substrates present fortuitously in the products. Questions remain unanswered, and further research is being planned to increase our knowledge base regarding oil spill bioremediation enhancement using commercial inocula.

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ALTERNATING CURRENT ELECTROCOAGULATION FOR  
SUPERFUND SITE REMEDIATION

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ABSTRACT

A study is being conducted by Electro-Pure Systems, Inc. (EPS) under the Emerging Technology portion of the U. S. Environmental Protection Agency's (EPA's) Superfund Innovative Technology Evaluation (SITE) Program to study alternating current electrocoagulation for Superfund site remediation. Alternating current electrocoagulation has proven to be effective in agglomerating and removing colloidal solids, metals and certain organic contaminants from surrogate soils prepared from the U.S. EPA's Synthetic Soil Matrix. Treatments under a wide range of operating conditions (power, electrode configurations, retention time, frequency, mode of operation) have enabled the optimum parameter settings to be established for multiple phase separation. Electrocoagulation enables appreciably enhanced filtration and dewatering rates to be realized for metals- and diesel fuel-spiked surrogate soil slurries; such enhancements are prompted by growth in the mean particle size of the clays and particulates from typically <10 microns to as much as 150 microns depending on the degree of electrocoagulation. Reduction in the total suspended solids content of clays in all slurries in excess of 90% can routinely be achieved. Bench-scale experiments of the metals-spiked surrogate soils indicate that electrocoagulation preferentially concentrates soluble metals into the sludge phase; excellent metals separation (Pb, Cr, Cu, Cd) can be realized. Experiments on surrogate wastes spiked with volatile organics suggest that this technology is not capable of effecting good volatile extractions from the aqueous phase. Reductions in excess of 80% in the total organic carbon (TOC) content of the diesel fuel-spiked surrogates can, however, be achieved.

Alternating current electrocoagulation is effective in reducing the volume of a potentially hazardous slurry by concentrating the clays and metals into a readily dewaterable and filterable solid phase. Electrocoagulation offers equivalent or slightly better treatment than chemical polymer addition and has the added attributes of producing more readily filterable sludges without introduction of soluble species. In terms of solids and metals reductions the results achieved by electrocoagulation are far superior to those achieved by alum addition.

This paper has been reviewed in accordance with the U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

Electro-Pure Systems, Inc. (EPS) has completed the first year of participation in the U. S. EPA's Emerging Technology portion of the SITE Program. The primary objective of this project is demonstration of the technical and economic viability of alternating current electrocoagulation technology for use in Superfund site remediation. Alternating current electrocoagulation offers a technologically simple mechanism to achieve phase separation of liquid-liquid and solid-liquid slurries and emulsions, to remove certain metals from solution and to destroy certain organic compounds. In the first year of the program laboratory experiments conducted in bench-scale electrocoagulation units, referred to as ACE Separators, were performed to evaluate performance of the technology for treatment of surrogate waste matrices containing metals and organic constituents that might be present at Superfund sites. The second year of the program entails investigation of the potential of a packed-bed catalyst version of the ACE Separator to oxidize organic compounds within aqueous phases. Presented in this paper is an overview of the technology, discussion of some preliminary results for the Year One SITE program and for testing of industrial effluents and a summary of the applications and benefits of ACE Separator usage.

## TECHNOLOGY DESCRIPTION

### BACKGROUND

Alternating current electrocoagulation (ACE Technology) was originally developed as a treatment technology in the early 1980s to break stable aqueous suspensions of clays and coal fines in the mining industry. The technology was developed as a replacement for primary chemical coagulant addition to simplify effluent treatment, realize cost savings, and facilitate recovery of fine-grained products that would otherwise have been lost. The traditional approach for treatment of such effluents entails addition of organic polymers or inorganic salts to promote flocculation of fine particulates and colloidal-sized oil droplets in aqueous suspensions. These flocculated materials are then separated by sedimentation or filtration. Unfortunately, chemical coagulant addition generates voluminous, hydrous sludges which are difficult to de-water and slow to filter. As an alternative to chemical conditioning and flocculation, ACE Technology agglomerates the particulates without adding any soluble species to produce a sludge with a lower contained water content and which will filter more rapidly. Another disadvantage of chemical coagulation is the high susceptibility to filter shear of the particulates and emulsion droplets entrained in the sweep flocs. Through separation of the hazardous components from an aqueous waste, the volume of potentially toxic pollutants requiring special handling and disposal can be minimized. Waste reduction goals may be accomplished by integrating this technology into a variety of operations which generate contaminated water. Laboratory-scale testing has also indicated the ACE Technology is capable of effecting removal of soluble and insoluble metals and anions from aqueous streams.

## PRINCIPLES OF ACE TECHNOLOGY

Most suspended solid particles carry electrical charges on their surfaces. Such charges commonly develop through preferential adsorption, ionization and isomorphous replacement. These ions form a primary layer which, in turn, attracts an oppositely charged secondary layer of ions. The size of the particles and the strength of the ionic charge largely affect whether the particles will aggregate and settle out of solution. When the particles are sufficiently large, gravity will usually overcome the electrical forces which tend to hold such particles in suspension. Smaller particles are more susceptible to being suspended by electrical forces. For example, if a particle has a weak ionic charge, the repulsive nature of the ionic double-layer will prevent the particles approaching close enough for Van der Waals forces to overcome the electrical repulsion. Thus, the particles are held in suspension.

ACE Technology is based upon colloidal chemistry principles using alternating current power and electrophoretic metal hydroxide coagulation. Two basic mechanisms have been postulated for enhancing particle growth characteristics as a result of electrocoagulation: electroflocculation, whereby minute quantities of highly-charged cationic metal hydroxides are released from the electrodes to facilitate flocculation, and electrostriction, whereby the charges on colloidal particles are neutralized when subjected to alternating current electrical field conditions. Electrostriction is believed to reduce the main stabilizing force of the suspension and the production of metal hydroxides assists in the flocculation and settling of the particles. ACE Technology prompts agglomeration of charge neutralized particles in a manner analogous to chemical polymerization resulting in an increase in the mean particle size of the solids and thus, ease of filtration from the aqueous phase. Each of these phenomena are discussed below.

### Electroflocculation

The theory of electroflocculation or metal ion flocculation is very well established. Iron and aluminum ions had been used for clarifying water as early as 2000 B.C. Parekh et al(1) developed a coagulation model involving use of metal hydroxides and fine particles. They reported that the optimum coagulation of a metal ion-particle system takes place at the iso-electric point of the metal hydroxide precipitate.

Electroflocculation causes an effect similar to that produced by the addition of chemical coagulants such as aluminum or ferric sulfate. These cationic salts destabilize colloidal suspensions by neutralizing negative charges associated with these particles at neutral or alkaline pH. This, in turn, enables the particles to come together in close enough proximity that Van der Waals attractive forces prompt their aggregation and settling with the neutral hydroxide floc. A report explaining electroflocculation chemistry was prepared by James F. Grutsh(2) for the American Petroleum Institute Committee on Environmental Control. Although the mechanism resembles chemical coagulation in that cationic hydroxide species are produced from the energized electrodes, the characteristics of the electrocoagulated floc often differ dramatically from those generated by chemical coagulation. They tend to be less hydrous, more shear resistant, and are more readily filterable.

## Electrostriction

The theory of electrostriction is little known and is based primarily on work done by Schwann.(3) Schwann examined the electrical properties of colloidal suspensions in electrolytes subjected to alternating current electric fields and discovered that colloidal suspensions exhibited variable, and often extremely high, dielectric constants (E) in alternating fields. Not only did the dielectric constant of the suspension decrease as the frequency was increased, but the dielectric loss factor (E") went through a maximum, and the conductivity (K) of the suspension increased dramatically (Figure 1). The peak of the dielectric loss factor curve appears at the characteristic frequency 'f' for the diagram, which is proportional to  $1/R^2$ , where R is the radius of spherical colloidal particles (for rod-shaped particles  $f \propto 1/R^3$ ). At the characteristic frequency, adsorbed ions, which give the colloidal particle a surface charge, are least tightly held, and can move freely over the particle surface in response to the electric field. For example, for particles of 3 microns size  $f = 60$  Hertz has been found to be optimum. Mixtures of particle sizes will broaden the 'f' band considerably. Theoretically, at a corresponding frequency the surface ion migration on a given sized particle continually leads its restabilizing time forming a continually shifting dipole (Figure 2). These polarized particles then can theoretically agglomerate under the force of mutual electrostatic attraction, rather than remain dispersed by the mutual electrostatic repulsion normal to colloidal aqueous suspensions. The degree to which electrostriction functions as a component of ACE Separator treatment is the subject of another ongoing study at EPS.

Within the ACE Separator the particulates and metal ions will move towards oppositely charged electrodes. Collisions are not only likely between positive and negative particles moving in opposite directions, but also between discharged particles of different sizes once the stabilizing charges are eliminated. Consequently, loosely-held particle surface charges near the characteristic frequency of the suspension could be neutralized and displaced by oppositely charged electrophoretically mobile ions, eliminating or greatly reducing the main stabilizing force of the suspension. Further collisions between now uncharged and/or partially charged particles could then create conglomerates which would eventually begin to move up or down in response to the relative density of the dispersing medium. The solution pH will change when highly mobile  $OH^-$  or  $H^+$  ions are used up to neutralize surface charges. Co-precipitation is also known to reduce concentrations of other materials in solution and suspension.

## ACE SEPARATOR OPERATION

The basic process of the ACE Technology is illustrated in Figure 3. The redistribution of charges and the onset of coagulation and flocculation occur within the ACE Separator through exposure to an alternating electric field. An ACE Separator contains electrodes in one of two design configurations: (1) a series of vertically oriented, parallel plates or (2) a series of stacked, cylindrical electrodes where a fluidized bed of metallic pellets is maintained. Residence time in the ACE Separator is typically less than 60 seconds, after which the flow is transferred to a gravity separation tank or to a filtration apparatus. Retention time in the ACE Separator may be reduced

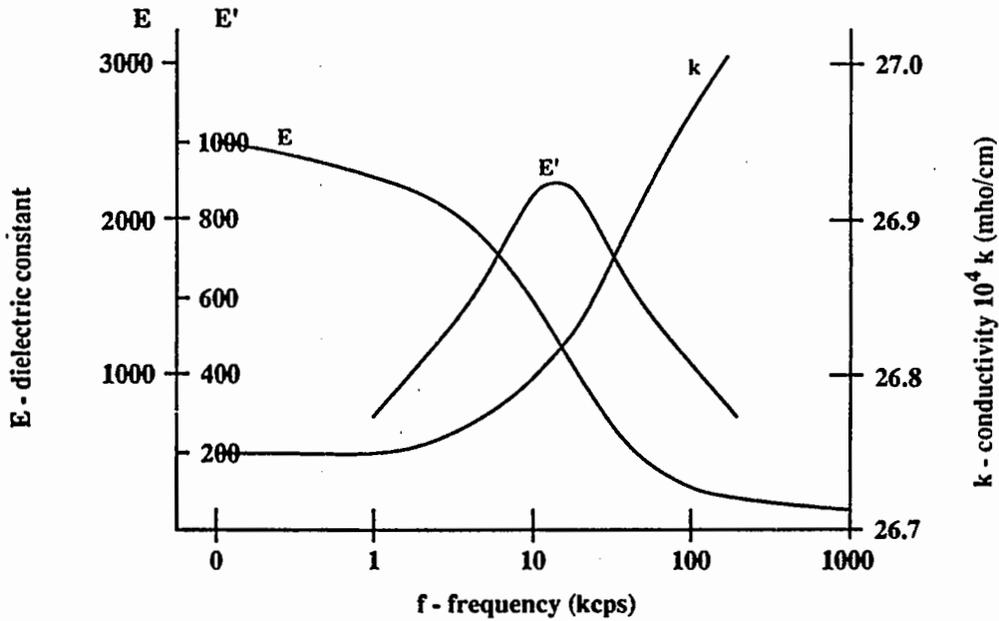


Figure 1. Effect of AC Power Frequency on Conductivity, Dielectric Constant and Dielectric loss Factor

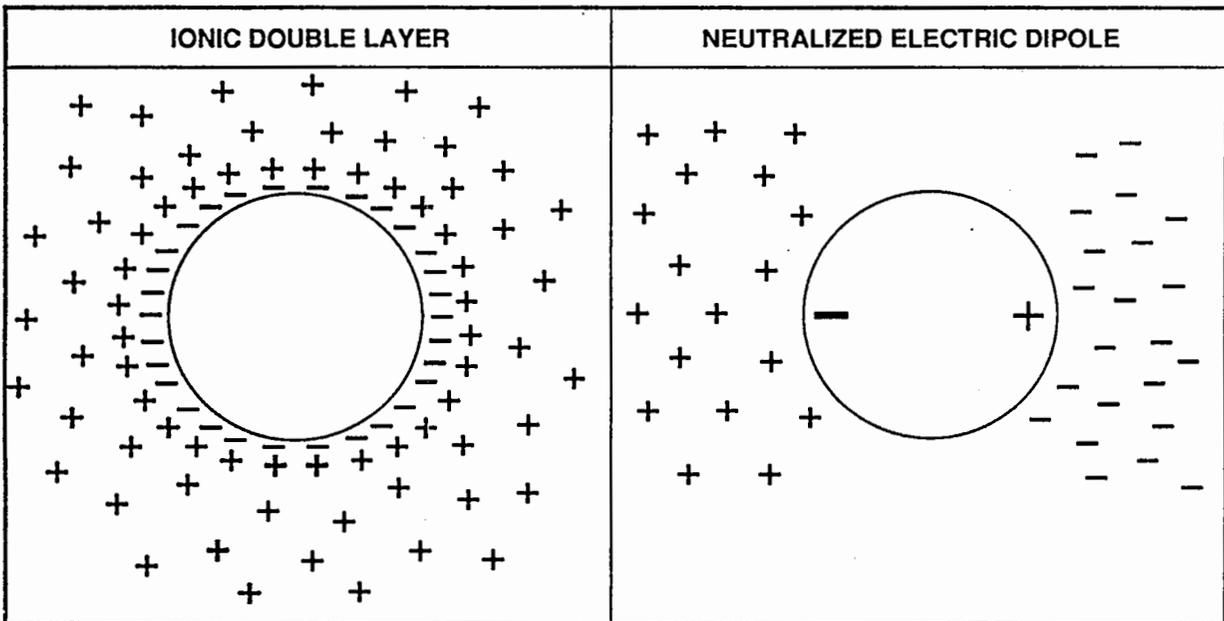


Figure 2. Illustration of Surface Charge Distributions On A Colloidal Particle

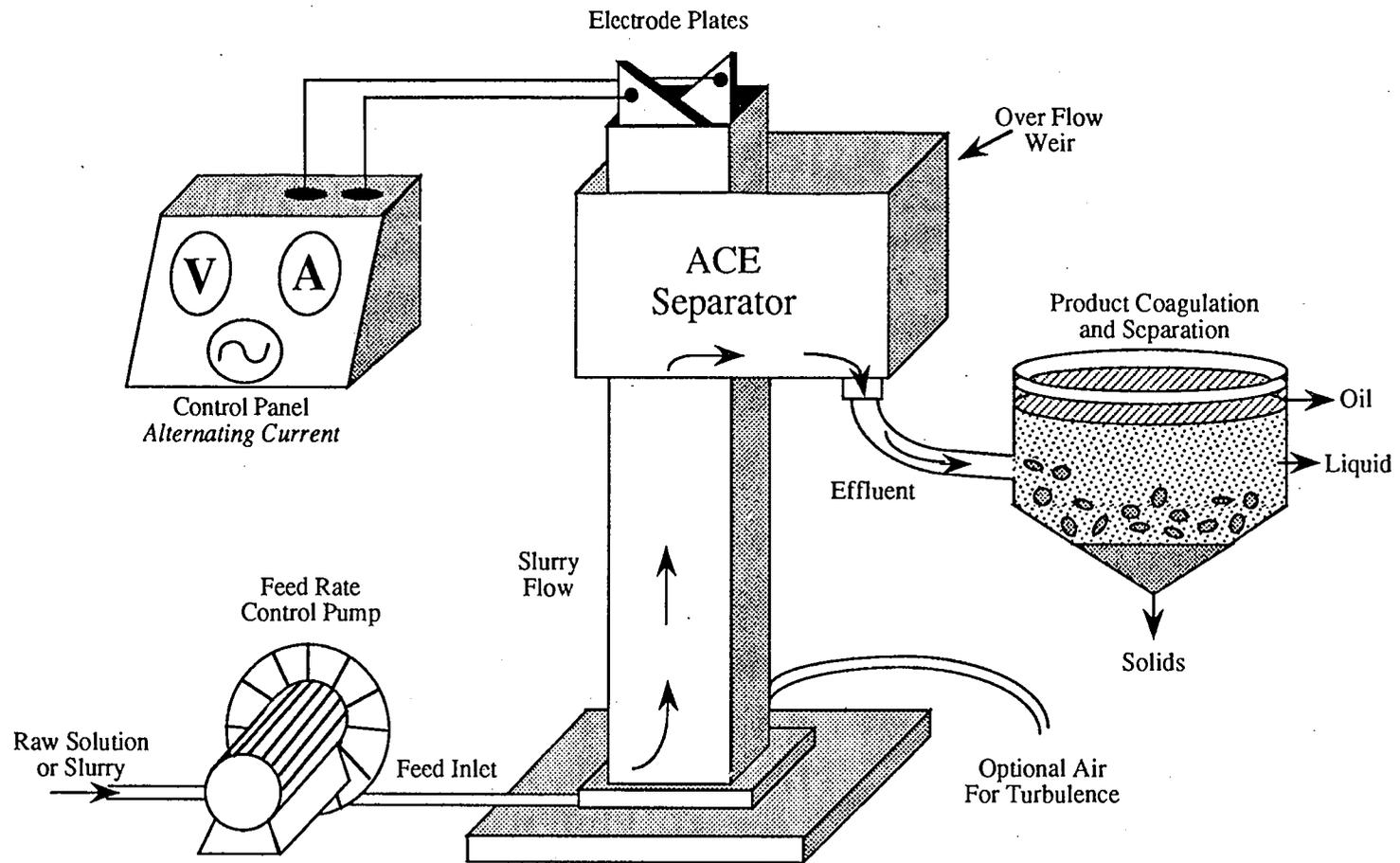


Figure 3. Schematic Diagram Of Ace Separator Unit

in many applications by adding turbulence to agitate the solution as it passes through the electric field. Turbulence is typically provided by bubbling air from the base of the unit; treatment of the vent gas may be necessary when volatile organics are involved due to air stripping effects. After separation, each phase (water, oil and solid) is removed for reuse, recycle, further treatment or disposal. The efficiency of electrostriction in removing capillary or interparticle absorbed water, as well as adhesion water between precipitated colloids, enhances the filtration characteristics of sludges.

Bench-scale tests and full-scale field applications performed by EPS as another study have demonstrated a phenomenon referred to as residual effectiveness whereby charge redistribution and coagulating forces appear to remain effective for extended periods of time. This phenomenon is important in that mixing and pumping of the solids or treated suspension can be accommodated after coagulation, if so dictated by other system design conditions, without losing the phase separation effectiveness.

The parallel electrode ACE Separator operates on low voltage (20-40V) and high current (50-500A) and for some applications, a frequency suited to the characteristics of the waste stream. The fluidized bed ACE Separator in contrast operates at a higher voltage (120-150V) and low amperage (0.5-5 amperes). ACE Separators of both designs operate at atmospheric pressure and are vented to alleviate any problems associated with gas accumulation. Solution characteristics such as particle size, conductivity, pH and chemical constituent concentrations dictate operating parameters of the unit (for example, electrode plate spacing, current density, frequency of power and chemical pre-treatment, if required). Quantity and flow rate will affect system sizing, retention time and mode of operation (recycle, batch, continuous).

#### EXPERIMENTAL DESIGN

Experiments were conducted on two surrogate wastes prepared from the EPA's Synthetic Soil Matrix. Both were prepared to be stable aqueous suspensions of silt, clay and top soil containing ~1% suspended solids, with or without spikes of toxic metals (Cd, Cr, Cu, Pb) or volatile organics (1,2-dichloroethane, ethylbenzene, tetrachloroethylene, xylenes). The first surrogate waste (Surrogate Waste A) contained solely the -40 mesh synthetic soil matrix fines while the second (Surrogate Waste B) incorporated both the fines fraction mixed with both 1.5% No. 2 diesel fuel and 1% of a strong surfactant (Titan TX-100).

A preliminary series of experiments was undertaken to investigate the effects of the five principal operating parameters of the ACE Separator: electrode plate spacing (field strength), residence (or treatment) time, applied current, current density and frequency of the applied current. These studies indicated that the higher the electrical field strength, applied current, retention time and current density (all of which correlate to higher aluminum introduction into the solution), the more effective the phase separation of the surrogate waste as judged by the clarity or suspended solids loading (TSS) of the treated solution supernate. Electrocoagulation was found to have a pronounced effect on the filtration rates of the slurries typically

yielding increases of 60-90%. The filter cake produced in all experiments was generally quite compact, readily cracked and less voluminous than that produced by comparative chemical treatments.

### EXPERIMENTAL RESULTS

#### CLAY SUSPENSIONS (SURROGATE WASTE A)

Surrogate Waste A was spiked with four metal salts ( $Pb(NO_3)_2$ ,  $CuSO_4 \cdot 5H_2O$ ,  $CdCl_2 \cdot 2 \frac{1}{2} H_2O$ ,  $CrCl_3 \cdot 6 H_2O$ ) at concentrations of 10-50 mg/l, thoroughly mixed and electrocoagulated at operating conditions found to be optimum for effecting separation of clays from the surrogate. While a majority of the soluble metals strongly adhere to the clays, electrocoagulation enables agglomeration of the colloidal, metal-bearing clays and significant >90% reductions in the soluble metals loadings (Table 1). The filtration time for the treated surrogate decreased to ~50% of that required for the untreated surrogate waste (3:02 minutes versus 6:00 minutes). Comparative chemical coagulant addition experiments with alum ( $Al_2(SO_4)_3$ ) and organic cationic polyelectrolyte flocculants (Drew Polymer 485) were also conducted on the surrogate waste. Electrocoagulation yielded a faster filtration rate (2:15 minutes for 100 mls) than for either the untreated slurry (7:30 minutes) or the alum-treated solution (3:53 minutes). Polymer treatment had the same filtration rate. Filter cake volume expressed as a percentage of the pre-filtered sludge volume seems to be a minimum for ACE Separator treatment (6%) compared to alum and polymer treatment (13-15%). The volume data indicate that the ACE Separator-treated solids cakes are more compact and easier to dewater than those for coagulant-treated samples. Particle size analyses of the treated and untreated slurries indicated that the mean size of the ACE Separator-treated solids both in the supernate and filtrate (25.2 and 35.1 microns, respectively) increased by a factor of 3-4 over that in the original slurry (9.1 microns). Larger particulate growth occurred as a result of electrocoagulation than by either polymer or alum addition (15 and 10 microns, respectively).

TABLE 1. SURROGATE WASTE A METALS-SPIKED EXPERIMENTS

ANALYTICAL PARAMETER	UNTREATED	ACE SEPARATOR TREATED		
	SLURRY (mg/l)	SUPERNATE (mg/l)	FILTRATE (mg/l)	FILTER CAKE (ug/g)
TOTAL SOLIDS	17,000	1,700	1,700	540,000
TOTAL SUSPENDED SOLIDS	22,000	25	3.0	N.A.
TOTAL ORGANIC CARBON	220	1.8	26	N.D.
TOTAL METALS:				
CADMIUM	7.9	0.89	2.2	340
CHROMIUM	16	0.074	0.018	1,100
COPPER	44	0.13	0.053	2,400
LEAD	32	0.11	1.7	2,700
MOISTURE CONTENT	N.D.	N.D.	N.D.	42.4

Spiking the surrogate waste with volatile organics at concentrations of 5-50 mg/l was undertaken to examine the effect of electrocoagulation on

volatiles extraction. Table 2 summarizes the results of one test. Significant loss of volatiles to the vapor phase during electrocoagulation appears to have occurred.

Comparison of the analytical data for supernate samples indicates pronounced reductions achieved for electrocoagulation. Not documented,

TABLE 2. SURROGATE WASTE A VOLATILE ORGANICS-SPIKED EXPERIMENTS

ANALYTICAL PARAMETER	UNTREATED SLURRY	ACE SEPARATOR TREATED		
		SUPERNATE	FILTRATE	FILTER CAKE
TOTAL SOLIDS (ug/g)	19,000	1,400	1,300	600,000
TOTAL SUSPENDED SOLIDS (mg/l)	13,000	41	<2	N.D.
TOTAL ORGANIC CARBON (mg/l)	150	2.4	3.2	N.D.
TOTAL CARBON (mg/l)	465	7.8	27	N.D.
ORGANIC CONTAMINANTS:				
1,2-DICHLOROETHANE (ug/l)	29,000	14,000	2,500	1.8
ETHYLBENZENE (ug/l)	5,900	1,700	590	<0.8
TETRACHLOROETHYLENE (ug/l)	6,900	1,300	390	1.5
XYLENES (total) (ug/l)	17,000	6,300	1,900	<5

however, was the loss of volatiles to the vapor phase as a result of stripping by the compressed air introduced into the ACE Separator to create turbulent conditions. Pronounced improvements in filtration rate for the ACE Separator-treated slurries (~3:00 minutes per 100 mls) compared to the untreated stock solution (>20:00 minutes per 100 mls) were again documented.

#### DIESEL FUEL CONTAMINATED SLURRY (SURROGATE WASTE B)

Electrocoagulation of the surrogate waste containing 1.5% diesel fuel produced effective reductions in suspended solids (112 to 12 mg/l), total carbon (230 to 110 mg/l) and total inorganic carbon (28 to 12 mg/l). Electrocoagulation of Surrogate Waste B spiked with metals (Cu, Cd, Cr, Pb) had respectable reductions (Table 3). For example, copper is reduced by 90-94%, cadmium and chromium by 91-97% and lead by 86-89%. No appreciable change in TOC loadings in the supernate resulted from treatment; the TSS was reduced by approximately 90% from 222 to 19 mg/l. Comparative chemical coagulant addition experiments were conducted for the diesel fuel contaminated slurry. The following generalizations can be made for the treatment: alum and polymer treatments generally require approximately 30% longer filtration times, ACE Separator and polymer treatments reduce the TS and TSS loadings to an equivalent degree, which is about 25% of the alum value, and better reductions in soluble metal concentrations were usually achieved with polymer and electrocoagulation treatment. Particle size data confirm the appreciable enhancement in the clay fraction as a result of electrocoagulation (Table 4).

The mean size of the ACE Separator-treated particulates both in the supernate and filtrate (188 and 20 microns, respectively) has increased by a factor of approximately 85 and 8, respectively, over that in the original slurry (2.2 microns).

TABLE 3. SURROGATE WASTE B METALS-SPIKED EXPERIMENTS

ANALYTICAL PARAMETER	UNTREATED	ACE SEPARATOR TREATED		
	SLURRY (mg/l)	SUPERNATE (mg/l)	FILTRATE (mg/l)	FILTER CAKE (ug/g)
TOTAL SOLIDS	1,870	1,480	N.D.	1,000,000
TOTAL SUSPENDED SOLIDS	222	4.5	N.D.	N.D.
TOTAL INORGANIC CARBON	15	7.8	N.D.	N.D.
TOTAL ORGANIC CARBON	130	6.6	N.D.	N.D.
TOTAL CARBON	150	20	1,300	N.D.
TOTAL METALS:				
CADMIUM	0.5	0.15	0.28	289
CHROMIUM	0.31	0.024	0.01	721
COPPER	0.30	0.085	0.44	650
LEAD	0.72	0.09	0.16	3,700

TABLE 4. DIESEL FUEL CONTAMINATED SURROGATE PARTICULATES SIZE DATA

TREATMENT METHOD	D(50%) SUPERNATE(microns)
Untreated Slurry	21.97
Polymer 425	7.91
Alum	9.32
ACE Separator	188.6

Analytical results for electrocoagulation of organic volatiles-spiked Surrogate Waste B slurries are similar to those for the clay suspension tests: marked improvement in filtration time (10:30 versus 31:00 minutes for 100 mls) and sizeable reductions in supernate TOC (91%), TSS (76-93%) and TC (86%) loadings. While electrocoagulation did appear to reduce the concentrations of the volatile organics in the supernate phase (Table 5), filtration of the reslurried supernate shears the solids to release many of the volatiles back into the aqueous phase.

With respect to the removal of the volatile organics, the concentrations of all four spiked species in the treated supernates are all lower than in the treated slurry. In contrast, the concentrations of these spikes in the filtrates were nearly all higher than in the untreated slurries.

#### SUMMARY OF SURROGATE TREATMENT RESULTS

ACE Separator treatment is effective in removing particulates from the soil suspensions (TS, TSS), in increasing their mean particle size and, consequently, in improving their filtration properties (speed of filtration). The technology has proven effective in reducing the metal concentrations in such slurries both by removing the clays to which metal ions have adsorbed and by coprecipitating soluble species. Reducing the loadings of TC, TIC, and TOC

attributable to fine particulates can be readily achieved; volatile organics are removed either by air stripping or by flocculation of the clays to which the organics have adhered. For volatile organics removal electrocoagulation is not a preferred treatment method.

TABLE 5. SURROGATE WASTE B VOLATILE ORGANICS--SPIKED EXPERIMENTS

ANALYTICAL PARAMETER	UNTREATED SLURRY	ACE SEPARATOR TREATED		
		SUPERNATE	FILTRATE	FILTER CAKE
TOTAL SOLIDS (ug/g)	10,900	867	N.D.	462,000
TOTAL SUSPENDED SOLIDS (mg/l)	5,050	47.5	97.3	N.A.
TOTAL ORGANIC CARBON (mg/l)	14,500	86.4	540	N.D.
TOTAL CARBON (mg/l)	11,700	220	4,450	N.D.
ORGANIC CONTAMINANTS:				
1,2-DICHLOROETHANE (ug/l)	4,900	1,500	3,800	110
ETHYLBENZENE (ug/l)	3,500	77	16,000	190
TETRACHLOROETHYLENE (ug/l)	3,900	120	15,000	170
XYLENES (total) (ug/l)	13,000	130	62,000	680

#### COMPLEMENTARY STUDIES

Several laboratory-scale amenability tests of industrial effluents have indicated that ACE Separator treatment is effective in removing certain metals, phosphate, fluoride, suspended solids and BOD from process waters.

#### PHOSPHATE REMOVAL

Three experiments on synthetic laboratory solutions and actual industrial wastewaters have confirmed the feasibility of phosphate removal by electrocoagulation. None of these experiments were optimized and so the extent to which phosphate could be reduced remains unknown. Treatment of wastewater from a commercial laundry reduced the phosphate concentration from 45 mg/l to 5.4 mg/l after minimal treatment (1.25 L, 0:45 min, 0.36 KW). Electrocoagulation of process water from a Florida phosphate mining operation reduced the  $PO_4$  level by 91% from 160 to 14 mg/l, once again with brief treatment (1.5 L, 0:10 min, 3.3 KW). Finally, treatment of a dilute phosphoric acid solution resulted in a pronounced conductivity decrease and pH increase suggesting phosphate removal by means of aluminum phosphate precipitation. Electrocoagulation should constitute an efficient method to remove orthophosphates from aqueous media; reduction of pyrophosphates and polyphosphates from wastewater may not, however, be as easily achieved.

## COD/BOD REDUCTION

Treatment of production vat wash waters from a manufacturer of imitation dairy products containing 0.1-1.0% total solids reduced the BOD loading from 3,530 mg/l to 343 mg/l, a 90% reduction. The filtration time for a 100 ml sample decreased from 15 minutes for an untreated sample to 0:50 minutes after ACE Separator treatment (7-8 amperes, 4 minute retention time), a 92% reduction.

## SYNTHETIC POLLUTANT METAL SOLUTIONS

Four synthetic solutions containing nickel, chromium (III), zinc and copper were prepared for electrocoagulation under a variety of pH, power and operating parameters. ACE Separator treatment at pHs typical of those for process wastewaters can routinely lead to >90% reduction in loadings of these four metals (Table 6).

TABLE 6. SYNTHETIC EFFLUENT STUDY METALS REDUCTIONS

EFFLUENT pH (units)	APPLIED POWER (KVA)	UNTREATED FILTRATE CONCENTRATION (mg/l)	ACE SEPARATOR FILTRATE CONCENTRATION (mg/l)	METAL REDUCTION (%)
COPPER				
6	2.0	127	3.4	97
8	0.7	110	0.85	99
10	2.4	17	1.1	93
CHROMIUM				
6	2.6	89	11	88
8	2.3	30	2.4	92
10	1.4	7.5	0.82	89
NICKEL				
6	2.0	127	3.4	97
8	0.7	110	0.85	66
10	2.5	17	1.1	94
ZINC				
6	2.2	138	30	78
8	2.4	1.5	0.55	64
10	0.2	6.6	0.56	92

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HIGH ENERGY ELECTRON BEAM IRRADIATION: AN EMERGING  
TECHNOLOGY FOR THE REMOVAL OF HAZARDOUS ORGANIC CHEMICALS  
FROM WATER AND SLUDGE - AN INTRODUCTION

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ABSTRACT

When high energy electrons impact an aqueous solution reactive transient species are formed. The three transient species of most interest are the aqueous electron,  $e^-_{aq}$ , the hydrogen radical, H·, and the hydroxyl radical, OH·. This paper describes preliminary research conducted at the Electron Beam Research Facility (EBRF) in Miami, FL to determine the removal efficiency for four organic chemicals, chloroform, trichloroethylene, tetrachloroethylene, benzene and toluene, using this innovative treatment process. The accelerator is a 1.5 MeV, 50 mA insulated core transformer type. The effect of water quality on the destruction of the organic compounds is examined using potable water, secondary wastewater and a secondary anaerobically digested sludge (2-5 % solids). Batch experiments can be conducted using 6,000 gallon tank trucks. The nominal treatment flow rate is 120 gallons  $\text{min}^{-1}$ . The absorbed dose can be varied from 0 to 800 krads.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

## INTRODUCTION

The ultimate disposal of toxic and hazardous organic chemicals is emerging as a priority in the search for new and innovative treatment technologies. By ultimate disposal we refer to the mineralization of the solutes of concern. Historically, for waste streams and even for site remediation, treatment process efficiency focused on the removal of the solute of interest. Little or no concern was voiced once the parent compound was "out of sight." In some cases the removal of the solute or waste product was considered complete by merely removing it from the manufacturing or remediation site to a landfill or by using deep well injection. These options are less attractive when considering the long term environmental effects and potential liability to the owner of the "disposed" waste. The "out of sight-out of mind" mentality is being called into question and it is probably safe to say will disappear in the future.

An extension of this approach is the use of carbon and aeration stripping, where the chemical(s) of interest are transferred to another media. In the case of carbon the solutes are concentrated and then are disposed of during the regeneration. If the carbon is not regenerated it then must be disposed of either in a landfill or by incineration. Aeration stripping for the removal of volatile chemicals, the cheapest alternative when using extremely naive and simplistic economic analyses, at worst transfers the problem to the air and at best transfers it to carbon or another adsorbent.

We feel that the more realistic solution to the problem of the disposal of toxic and hazardous organic waste chemicals will be treatment processes that result in, or facilitate, the mineralization of the chemicals. Probably the best known process to achieve this is the use of ozone,  $O_3$ , most often in the presence of various catalysts for its decomposition, e.g. ultraviolet (UV) light and/or hydrogen peroxide,  $H_2O_2$ . Other chemical/physical processes that are receiving attention are supercritical oxidation and wet oxidation. Bioremediation can also be considered an ultimate disposal process. Incineration of wastes has certain demonstrated advantages, but also a high potential for the formation of reaction by-products that may be as bad or worst than the starting materials. Thus, this technology is now under critical review when suggested as the process of choice.

This paper describes an innovative treatment process for the ultimate disposal of toxic and hazardous organic chemicals in aqueous solutions. The underlying chemistry is reviewed to acquaint the reader with the process and the technology of using high energy electron irradiation. Experimental results are presented for five compounds of interest in site remediation.

## ELECTRON BEAM TECHNOLOGY

Electron beams have been in commercial use since the 1950s. Early applications involved the cross-linking of polyethylene film and wire insulation. The number of applications has since grown to include sterilization of medical supplies, rubber vulcanization, disinfection of wastewater, food preservation, curing of coatings, etc. Today

there are several hundred electron processing systems installed for industrial applications in over 25 countries.

Polymerization of cable insulation and cross-linking of plastic film still account for the bulk of the applications. More than half of the total installed world capacity of 15 MW of electron beam power is devoted to these applications while less than 1 MW is used for sterilization of medical products. Only a small amount of the installed capacity is used for biological disinfection and detoxification (1). The reasons for the relatively slow growth in the latter applications can only be partially explained by need and economic considerations, and yet these applications hold the potential for the most social good (2).

Electron beam processing involves exposing the material to be irradiated to a stream of high energy (fast) electrons. These electrons interact with the material in less than  $10^{-12}$  seconds to produce electrons of lower and lower energy. Eventually a large number of slow electrons with energies less than 50 eV is produced, and these electrons interact with molecules to produce excited states of these molecules, positive ions and electrons. Eventually the electrons slow to thermal energies and get trapped. In materials of low dielectric constant most electrons do not escape the pull of the positive ions formed when they were produced. The electrons are attracted back to the positive ions causing a chemical reaction. This is termed direct radiolysis. In high dielectric materials such as water and aqueous solutions, most electrons escape the pull thus leaving both the positive ions and electrons free to react with the water or waste components in it. This is referred to as indirect radiolysis. The ratio of direct to indirect radiolysis in wastewater is approximately the weight fractions of waste to water (3). The radiation chemistry of aqueous solutions is presented in more detail in another section of this paper.

### ELECTRON BEAM RESEARCH FACILITY

The Electron Beam Research Facility (EBRF) is located at the Miami-Dade Central District Wastewater Treatment Plant located on Virginia Key, Miami, Florida. Schematic diagrams of the EBRF are shown in Figures 1 and 2. The facility consists of a horizontal 1.5 MeV electron accelerator. The accelerator is an insulated-core transformer (ICT) type, capable of delivering up to 60 mA beam current. However, we usually use 50 mA as the upper limit in beam current. Varying the beam current changes the absorbed dose in a linear fashion, allowing for experimentation at doses from 0 to 800 krads. The electron beam is scanned at 200 Hz to give a coverage of 48" wide and 2" high.

Influent streams at the EBRF are presented to the scanned beam in a falling stream approximately 48" wide and at the design flow of 120 gpm is 0.15" thick. Since the maximum penetration in water is approximately 0.29" for 1.5 MeV electrons, some electrons pass through the stream and thus not all of the beam energy is transferred to the water. With the addition of overscanning the waste stream to insure that the edges of the stream are irradiated, more energy is lost with the result that the efficiency of energy transfer is approximately 60 - 85% (see section on electron utilization efficiency). Thus when the

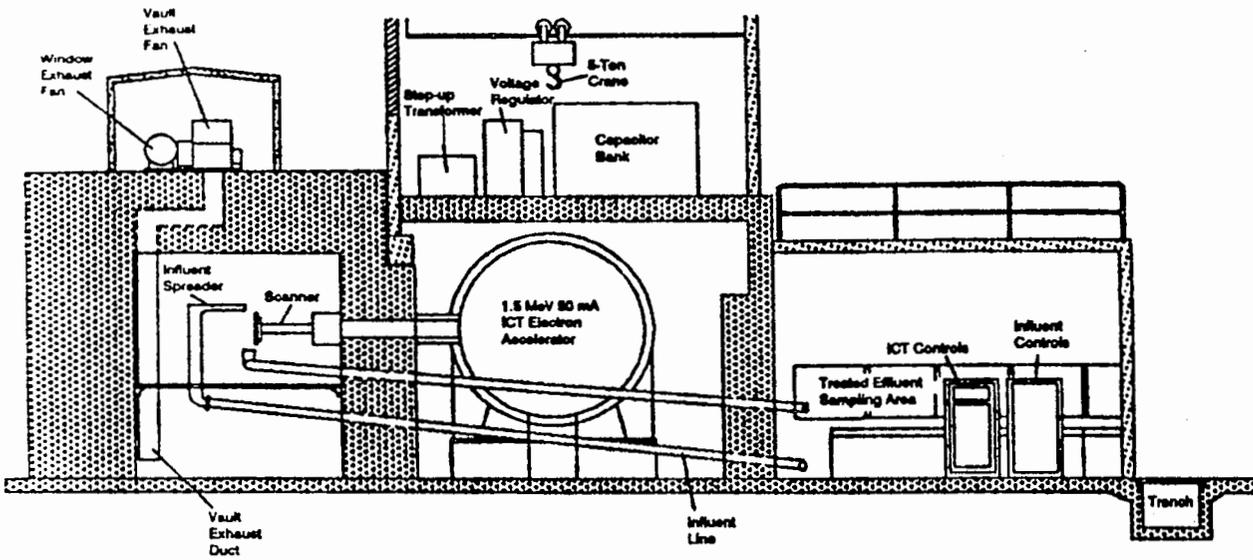


Figure 1. Schematic diagram of electron beam research facility, ground view.

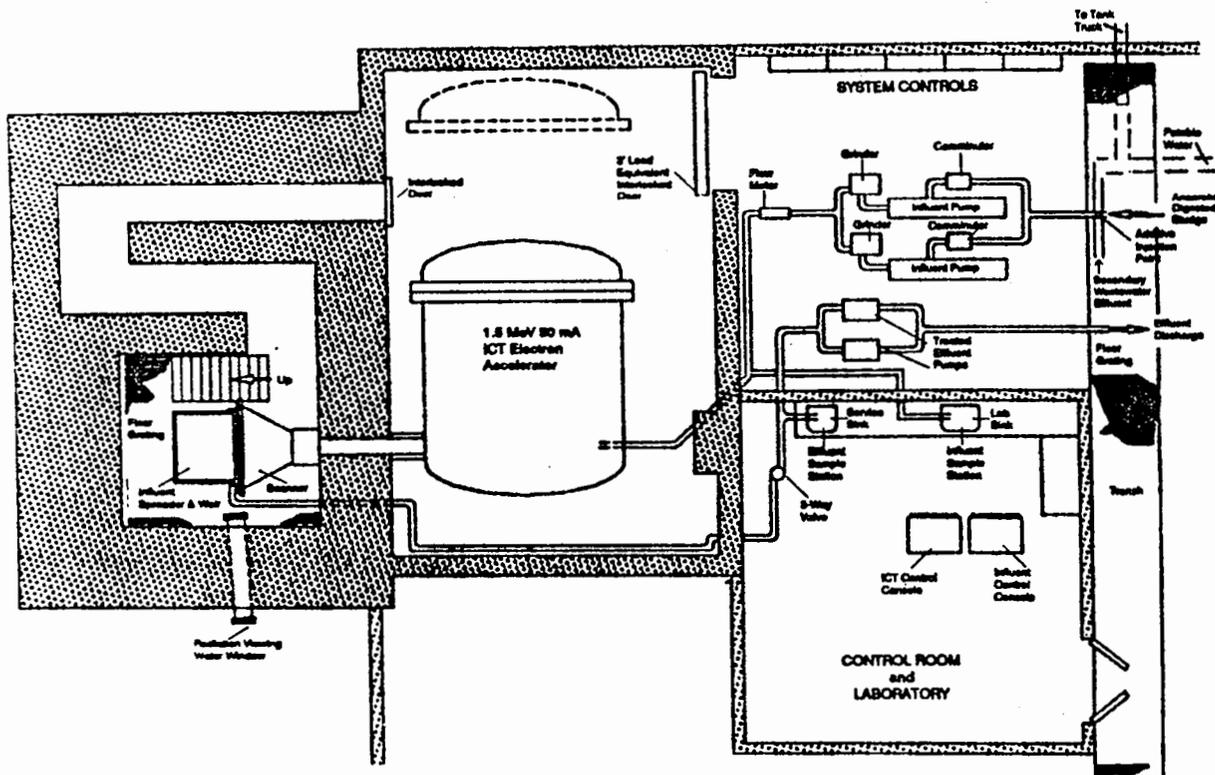


Figure 2. Schematic diagram of electron beam research facility, top view.

electron beam is operating at 50 mA (75 kW) the waste stream is receiving an average dose of approximately 650 krads. Total power consumption, including pumps, chillers and other auxiliary equipment is about 120 kW.

Because the system is being used for research, and water quality is one of the main experimental variables, three influent streams are directly connected to the facility. These three influent streams are potable water, chlorinated secondary wastewater and secondary anaerobically digested sludge that is 2-5% in solids. Batch experiments can be run at the facility utilizing a 6000 gallon tank truck connected to the influent pump. Experiments have been conducted using raw wastewater collected and transported in the tank trucks.

The EBRF is instrumented with resistance temperature devices (RTDs) to obtain direct estimates of absorbed dose. Five RTDs are mounted in the influent (2 sensors) and effluent (3 sensors) streams immediately before and after irradiation. The RTDs are connected via an interface to a computer which continuously reads and records temperatures and the absorbed dose is estimated by converting the observed temperature differences to the energy transferred to the water. The average absorbed dose ( $D_{AV}$ ) in pure water is calculated using the equation:

$$D_{AV} = K(t_2 - t_1) \quad [1]$$

where,  $t_1$  and  $t_2$  are the before and after irradiation water temperature of the flowing stream in °C, respectively; and K is the constant of proportionality:

$$K = 418 \text{ krads } ^\circ\text{C}^{-1}. \quad [2]$$

Therefore, an increase 1°C in water temperature is equivalent to a dose of 418 krads in pure water.

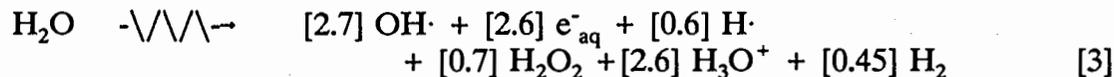
During experiments to determine the removal efficiency of parent compounds and to collect samples to determine reaction by-products, samples are taken prior to and after irradiation. These samples are obtained in the control room from continuously running sample streams.

## AQUEOUS CHEMISTRY OF HIGH-ENERGY ELECTRONS

The purpose of this section is to provide a brief overview of aqueous-based radiation chemistry. This brief introduction should assist the reader in understanding the application of high energy electron irradiation to the treatment of toxic and hazardous organic wastes in water and sludge.

The studies reported in the literature relating to radiation chemistry have been conducted in pure aqueous solutions. The extrapolation of pure water data to natural waters is complicated by the presence of inorganic and organic matter (primarily humic substances) found in natural waters. These compounds may interact with the transient reactive species formed during irradiation and lead to side reactions not observed in pure water. An example is the reaction of hydroxyl radical with carbonate ions, similar to that observed in processes utilizing  $O_3$ .

High-energy electron irradiation of pure water results in the formation of electronically excited states and/or free radicals along the path of the electron.  $10^{-9}$  sec after the electron has passed through a solution the products that are present are shown in Equation [13] (4-8):



Unlike photochemical reactions where one photon of light initiates one (molecular) reaction, a high energy electron is capable of initiating several thousand reactions as it dissipates its energy. The efficiency of conversion of a high energy electron, ionizing radiation, to a chemical process is defined as G (shown in brackets in Equation 13). G is the number of radicals, excited states or other products, formed or lost in a system absorbing 100 eV of energy. Of the products formed in Equation [13], the most reactive are the oxidizing, hydroxyl radical (OH·), and the reducing, aqueous electron (e<sub>aq</sub><sup>-</sup>) and hydrogen radical (H·). Thus, the chemistry of primary interest in the high energy electron irradiation process is that of these three species.

### CONCENTRATION OF REACTIVE SPECIES

One aspect of the research on high energy electron irradiation of toxic organic chemicals is to develop an understanding of the underlying chemistry. This understanding would be helpful in predicting, *a priori*, the success of the process for various applications. It is possible, using absorbed dose and G values (equation 13), to determine the approximate concentration of the transient reactive species in irradiated aqueous solutions. For a chemical with a G = 1, and a dose of 1 Mrad the concentration of the reactive species is  $1.04 \times 10^{-3}$  mole L<sup>-1</sup> or 1.04 mM (16).

Thus, for a G value of 2.7, e.g., OH· from equation 1, and an absorbed dose of 1 Mrad, there are 2.81 mmol of OH· formed. Typical concentrations of these transient reactive species and H<sub>2</sub>O<sub>2</sub>, at several doses, are summarized in Table I.

TABLE I. ESTIMATED CONCENTRATION OF TRANSIENT REACTIVE SPECIES AT SEVERAL DOSES USING HIGH ENERGY ELECTRON IRRADIATION

DOSE (krads)	e <sub>aq</sub> <sup>-</sup>	H·	OH·	H <sub>2</sub> O <sub>2</sub>
		mM		
100	0.27	0.06	0.28	0.07
500	1.4	0.3	1.4	0.4
1000	2.7	0.6	2.8	0.7

## RADICAL SCAVENGER EFFECTS

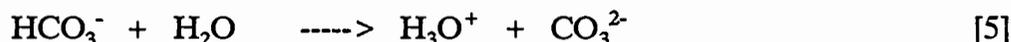
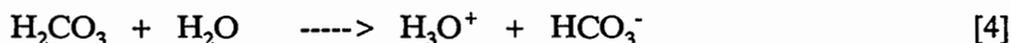
An important consideration in extending laboratory data to natural waters is the effect of naturally occurring radical scavengers. In this section we will present an overview of some of the scavengers for which rate data exist. A limitation is the lack of rate constants for inorganic constituents commonly found in natural waters.

### OXYGEN

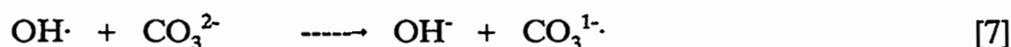
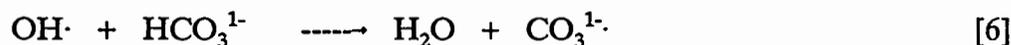
Both  $e_{aq}^-$  and  $H\cdot$  rapidly reduce  $O_2$  to form  $O_2^-$  ( $pK_a = 4.8$ ) with second order rate constants of  $1.9 \times 10^{10}$  and  $2.1 \times 10^{10} M^{-1} s^{-1}$ , respectively (12). Using a dissolved oxygen concentration of  $3.7 \text{ mg L}^{-1}$  (0.12 mM). At a dose of 100 krad this  $O_2$  concentration would remove approximately 35% of the two reactive species. However, at 800 krad only 5% would be removed.

### BICARBONATE/CARBONATE ION

A common  $OH\cdot$  scavenger in natural waters is alkalinity. Alkalinity, the measure of the total carbonate concentration is further complicated by the equilibrium that exist in natural waters.



Based on the pH and equilibrium calculations the carbonate/bicarbonate ion distribution is quite different in the waters used for study at the EBRF. For example, the secondary wastewater has a pH = 7.0 whereas the potable water is approximately 9.0. The relative effects of these ions on radical scavenging can be calculated from the equations:



and, the second order reaction rate constants. The second order rate constants are  $8.5 \times 10^6 M^{-1}s^{-1}$  and  $3.9 \times 10^8 M^{-1}s^{-1}$ , respectively (9).

More specifically, the two water sources at the EBRF were used to calculate the relative effects of alkalinity on  $OH\cdot$  concentration. The alkalinity of the secondary wastewater, pH = 6.78, and the potable water, pH = 8.64, in one set of experiments was 1900 and 360  $\mu M$ , respectively. Although the alkalinity of the secondary wastewater was 5-fold higher than the potable water, the  $OH\cdot$  scavenging is approximately 2.5 times higher in the potable water based on bicarbonate/carbonate equilibria. This relationship was determined by summing the product of the concentration of the carbonate and bicarbonate ions with  $OH\cdot$  reaction rate constants in each water.

The reaction of the carbonate radical ion,  $\text{CO}_3^{\cdot-}$ , is not known for many solutes, and therefore this process is considered as a loss of reactive species with no removal of solute. It is possible that the removal efficiency would be effected by the presence of this radical, and further studies are necessary to determine the effects.

## NITRATE ION

When comparing the removal of solutes in potable water and secondary wastewater, the presence of higher concentrations of nitrate ion ( $\text{NO}_3^{1-}$ ) in the secondary wastewater may effected solute removal efficiency by acting as an  $e_{(aq)}^-$  scavenger. By efficiently scavenging  $e_{(aq)}^-$  the effective concentration of the  $\text{OH}\cdot$  might be increased (minimizing recombination of the  $e_{(aq)}^-$  and  $\text{OH}\cdot$ , thereby increasing the effective  $\text{OH}\cdot$  concentration) and removal enhanced. No information is available on the reactions of the nitrate radical ( $\text{NO}_3\cdot$ ) with the solutes in this study.

## DISSOLVED ORGANIC CARBON

Another common component in natural waters is the ill-define fraction referred to as dissolved organic carbon, DOC. The difference in DOC concentration in secondary wastewater (6-fold higher than the potable water we used for our studies) may have also reduced removal efficiency by acting as an  $\text{OH}\cdot$  radical scavenger. There are no data on the reactions of either  $e_{aq}^-$  or  $\text{H}\cdot$  with DOC and only indirect evidence of the reaction with  $\text{OH}\cdot$ .

## METHANOL

An experimental artifact for much of the data obtained at the EBRF results from the need to use methanol as a carrier of the organic solutes of interest. Based on the ratio of the injection pump flow rate to the aqueous stream flow rate, the concentration of methanol for all experiments was approximately 3.3 mM. Methanol reacts with  $\text{OH}\cdot$ , and to a lesser extent with  $\text{H}\cdot$ , in aqueous solution with second order reaction rate constants of  $9.7 \times 10^8$  and  $2.6 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ , respectively (9). Therefore, under the experimental conditions employed, the removal efficiency of the solutes is probably underestimated relative to aqueous solution of the solutes in the absence of methanol, due to  $\text{OH}\cdot$  scavenging.

## EXPERIMENTAL RESULTS FOR THE REMOVAL OF TOXIC AND HAZARDOUS ORGANIC CHEMICALS IN AQUEOUS SOLUTION

We have conducted numerous experiments on organic chemicals that may be of interest in: water treatment, trihalomethanes; groundwater contamination, halogenated ethanes and ethenes; leaking underground storage tanks, benzene and substituted benzenes; as well as other organic chemicals now regulated as hazardous wastes. Results for selected compounds will be reviewed below. The six compounds are representative of the major groups mentioned above.

## TRIHALOMETHANES

One of the initial chemical groups studied at our facility was the halogenated methanes. Others have reported studies using electron and gamma irradiation of aqueous solutions of chloroform (10, 11). We have studied  $\text{CHCl}_3$  and  $\text{CHBr}_3$  and observed removal efficiencies of  $\text{CHCl}_3$  of approximately 85 - 99.9% in secondary and raw wastewater, and potable water, respectively.

The removal of  $\text{CHCl}_3$  is effected by water quality. That is, in potable water we observed >99% removal at 800 krads and initial concentrations of between 75 - 750  $\mu\text{g L}^{-1}$  (Figure 3). Similar initial concentrations in secondary and raw wastewater resulted in the removal of approximately 85 - 90% (Figures 4 and 5). To achieve higher removal efficiencies either higher doses would be required or, the water would have to be recirculated a second time.

The removal efficiency of  $\text{CHBr}_3$  in raw wastewater and potable water is not affected by the change in water quality and is independent of concentration in the range of 100 - 1500  $\mu\text{g L}^{-1}$  and above 100 krads is >99.99% (16).

The reaction by-products have not been studied in detail as yet. However, in studies conducted at low solute concentrations, none of the halogenated reaction by-products shown in the mechanism equations 45 - 60 have been observed. The liquid-liquid extraction method used for the quantification of the  $\text{CHCl}_3$ , would also have determined the presence of the chlorinated ethanes at detection limits of 0.01  $\mu\text{L}^{-1}$ . Research is now underway to determine the reaction by-products, aldehydes and carboxylic acids.

## HALOGENATED ETHENES

Another group of organic chemicals that have been studied at our treatment facility are the halogenated solvents. The compounds most commonly found are trichloroethylene (TCE) and tetrachloroethylene (PCE) (12). We have shown that the removal efficiency of both compounds, in potable water, is >99.9%, at doses of approximately 800 krads. The removal of TCE and PCE from secondary wastewater is 90 - 95% at 800 krads. Thus, as we observed for  $\text{CHCl}_3$ , water quality does affect removal efficiency of these two compounds.

Figures 6 and 7 show results of the removal of these two compounds at several doses in potable water and secondary wastewater. No studies have been conducted to examine the variables of solute concentration. However, we expect that results similar to those obtained for  $\text{CHCl}_3$  will be obtained when the experiments are completed. Although no studies have been conducted to examine the reaction by-products, the analyses of TCE and PCE involve liquid-liquid extraction, and no halogenated reaction products have been observed during the chromatographic determinations.

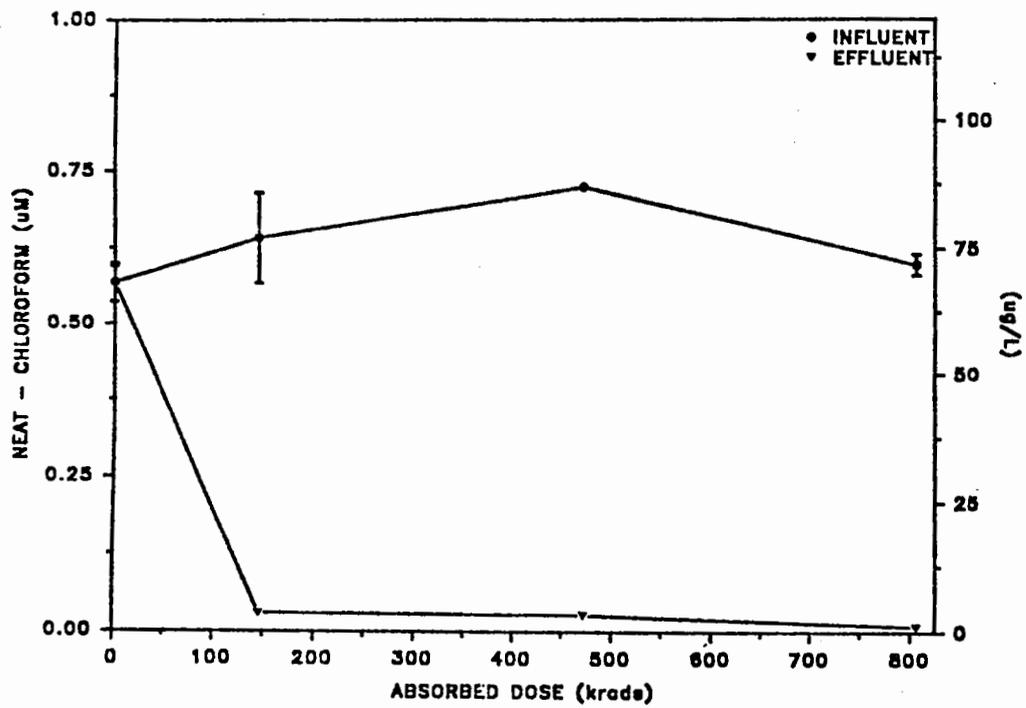


Figure 3. Removal of chloroform at several irradiation doses in potable water at two initial concentrations (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point).

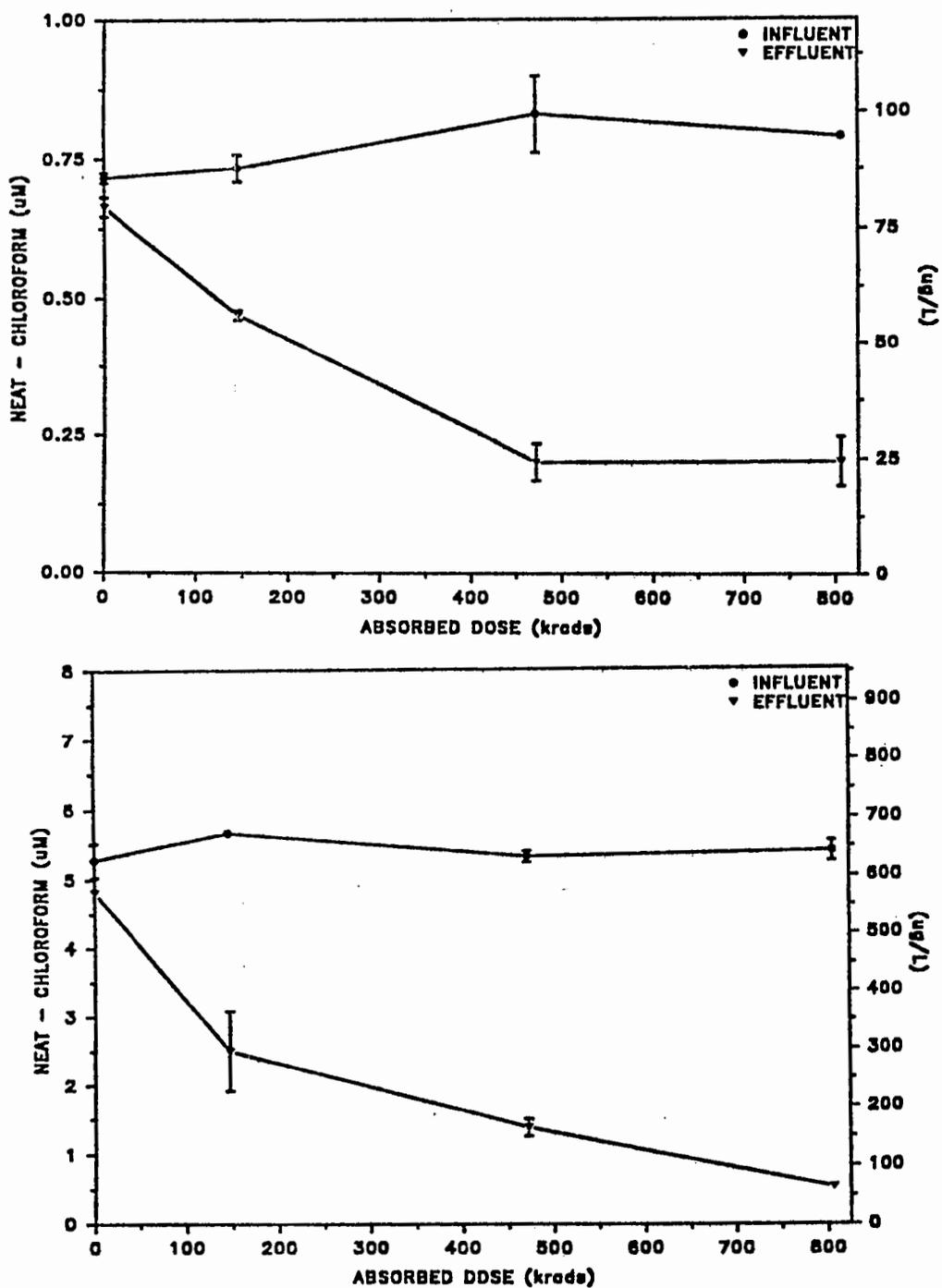


Figure 4. Removal of chloroform at several irradiation doses in secondary wastewater at two initial concentrations (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point).

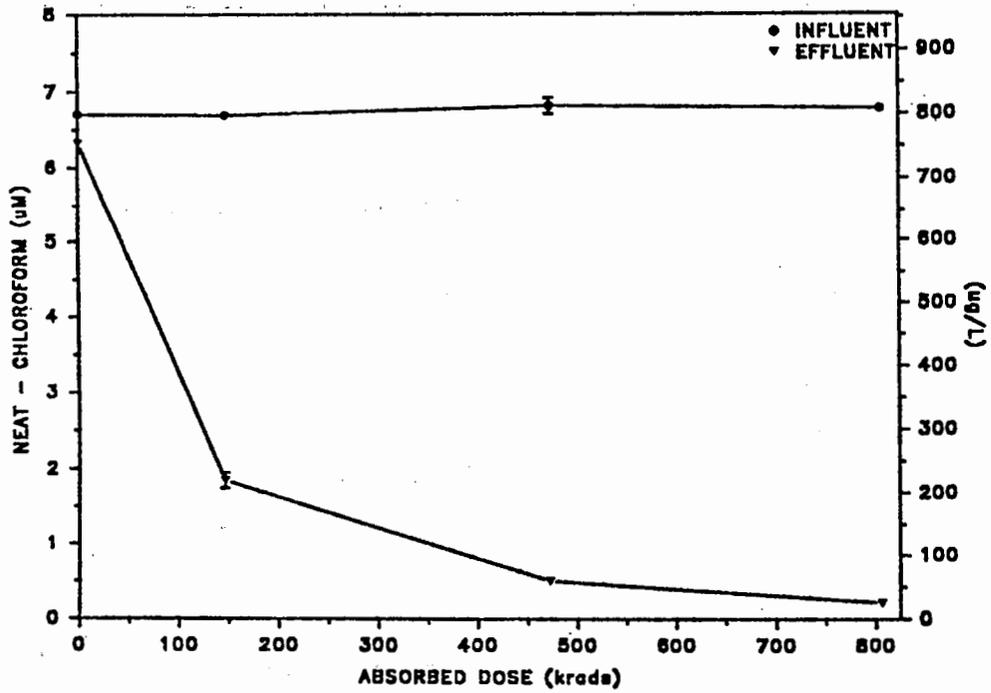
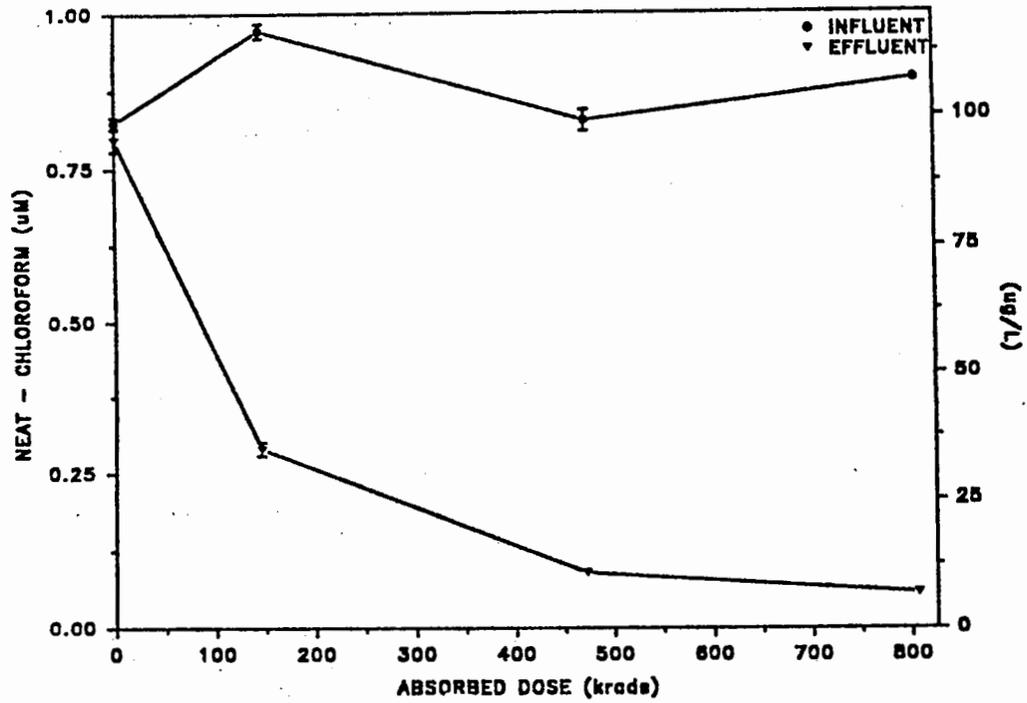


Figure 5. Removal of chloroform at several irradiation doses in raw wastewater at two initial concentrations (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point).

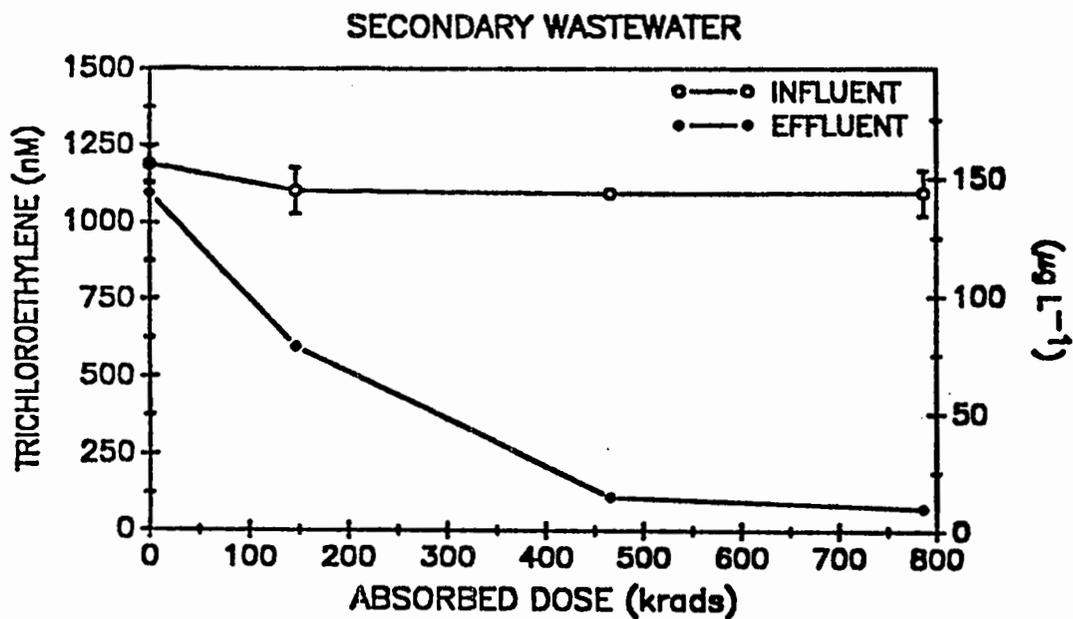
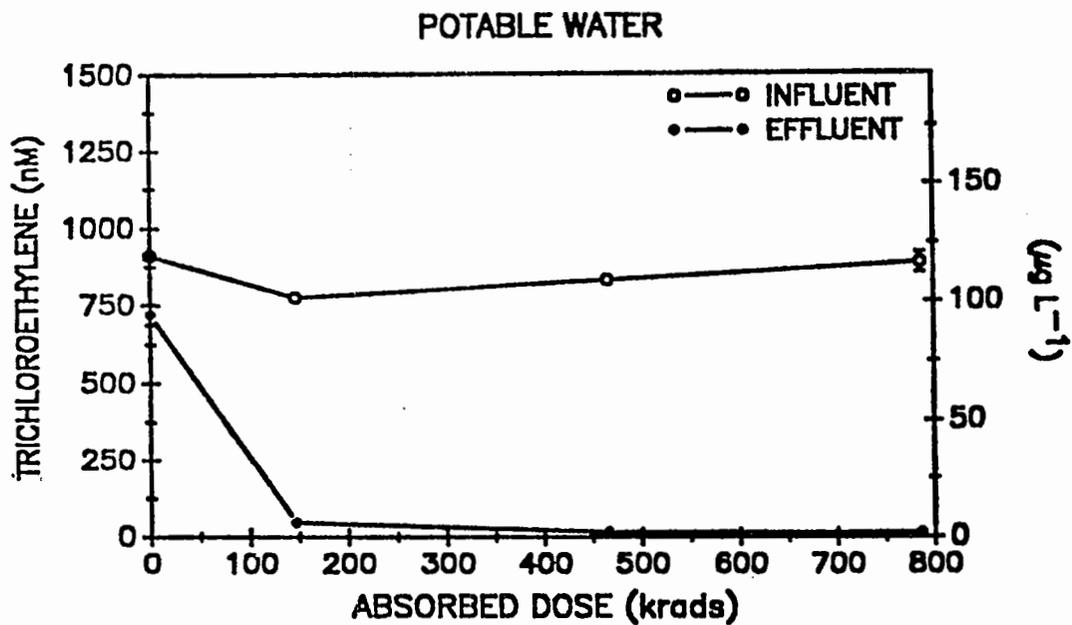


Figure 6. Removal of TCE at several irradiation doses in potable and secondary wastewater (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point).

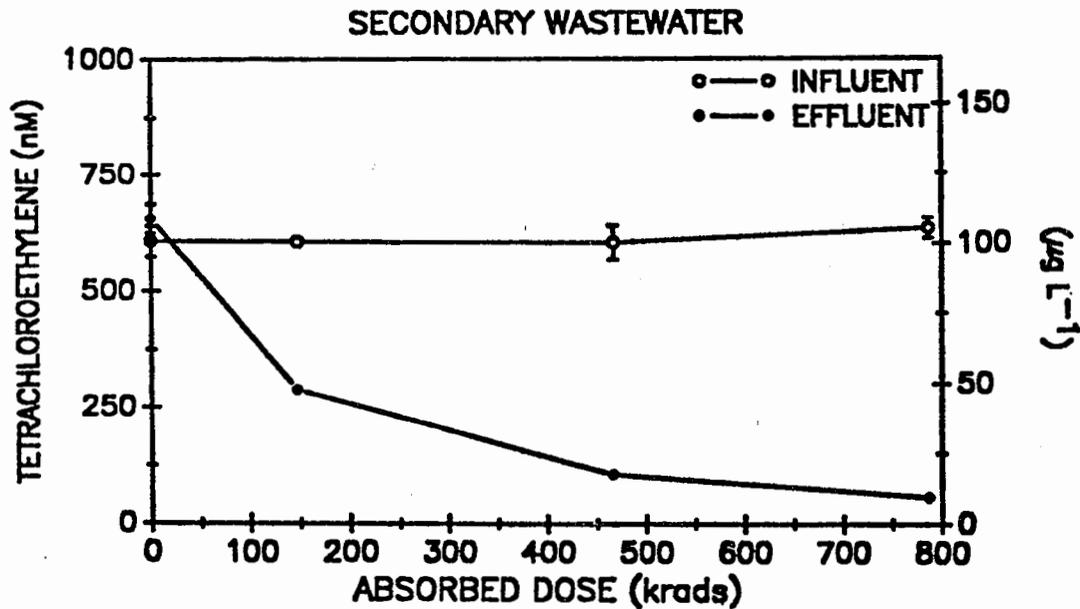
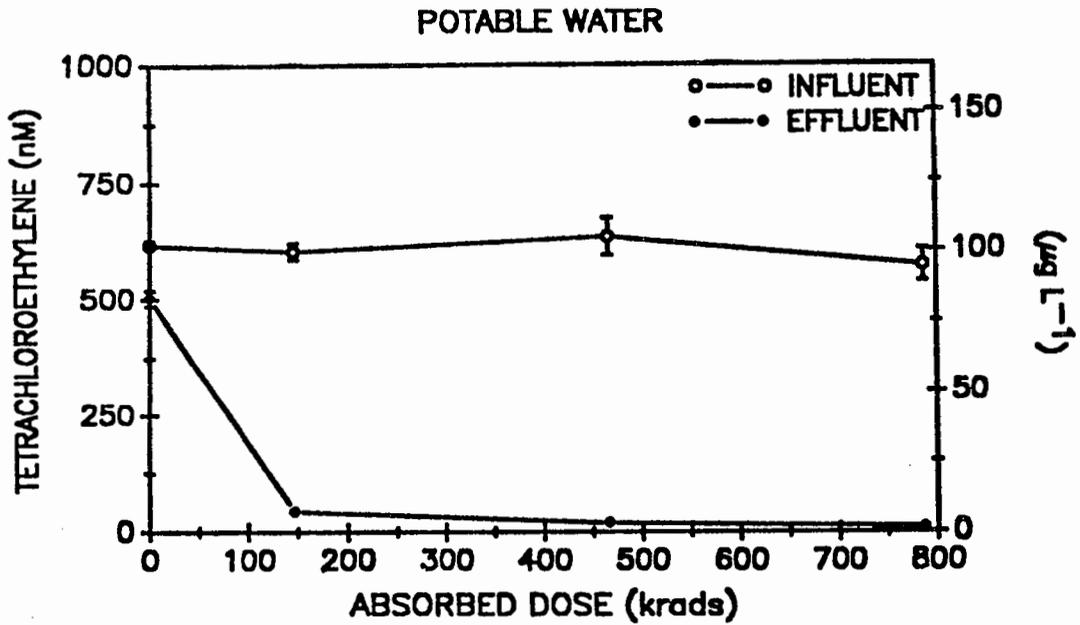


Figure 7. Removal of PCE at several irradiation doses in potable and secondary wastewater (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point).

## BENZENE AND SUBSTITUTED AROMATIC COMPOUNDS

A third group of compounds which we have studied are benzene and substituted benzenes (13, 14).

Figure 8 shows the effective removal of benzene and toluene from potable water. Three experimental factors affected removal efficiency: water quality, solute concentration, and dose. Both compounds were removed to below detection limits in potable water when added at the lower initial concentration. However, in the secondary wastewater, at the lower solute concentration, 90 - 96% removal was observed for all four solutes at 787 krads.

Concentration effects were also examined by irradiating mixtures with solute concentrations approximately 20 times higher in concentration. For example at 0.96  $\mu\text{M}$  ( $75 \mu\text{g L}^{-1}$ ) removal of benzene to below detection limits ( $0.01 \mu\text{g L}^{-1}$ ) was observed in potable water while at 17.5  $\mu\text{M}$  ( $1370 \mu\text{g L}^{-1}$ ) the benzene was reduced by 93%, at an absorbed dose of 787 krads. Similar results were observed for toluene in both potable water and secondary wastewater.

The G value for solute removal at a given dose,  $G_d$ , is defined by the disappearance of the solute in aqueous solutions, and is determined experimentally using the following equation:

$$G_d = \frac{([\text{org}]_d)(6.02 \times 10^{23})}{(d)(6.24 \times 10^{17})} \quad [8]$$

where,  $[\text{org}]_d$  is the change in organic solute concentration in  $\text{mol L}^{-1}$  at a given dose,  $d$  is the dose in krads,  $6.24 \times 10^{17}$  is the constant to convert krads to molecules  $\text{L}^{-1}$ , and  $6.02 \times 10^{23}$  is Avogadro's number.

The  $G_d$  values at all doses for potable water were very similar to those observed in the secondary wastewater at the low solute concentration (Table II). At the high solute concentration, the  $G_d$  values in potable water were higher when compared to secondary wastewater, only at the lowest dose. At the two higher doses the  $G_d$  values were very similar in both waters, with the exception of benzene where the  $G_d$  value appeared to be higher in potable water. At the higher solute concentrations the observed  $G_d$  values were an order of magnitude higher than those observed for low solute concentrations. This observation is consistent with removal being first order in solute concentration.

A plot of  $\ln [\text{solute}]$  against dose for both compounds was linear in potable water and secondary wastewater. Table VII summarizes the observed dose constants and half-dose ( $d_{1/2}$ ) for benzene and toluene in potable water and secondary wastewater at two solute concentrations.

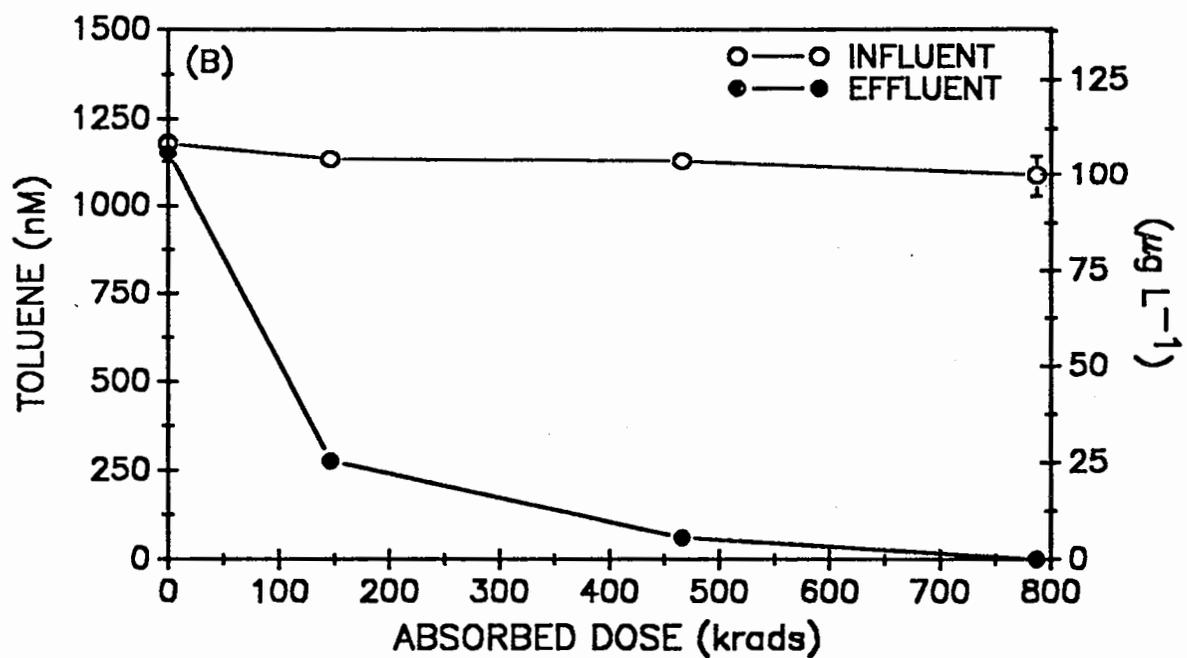
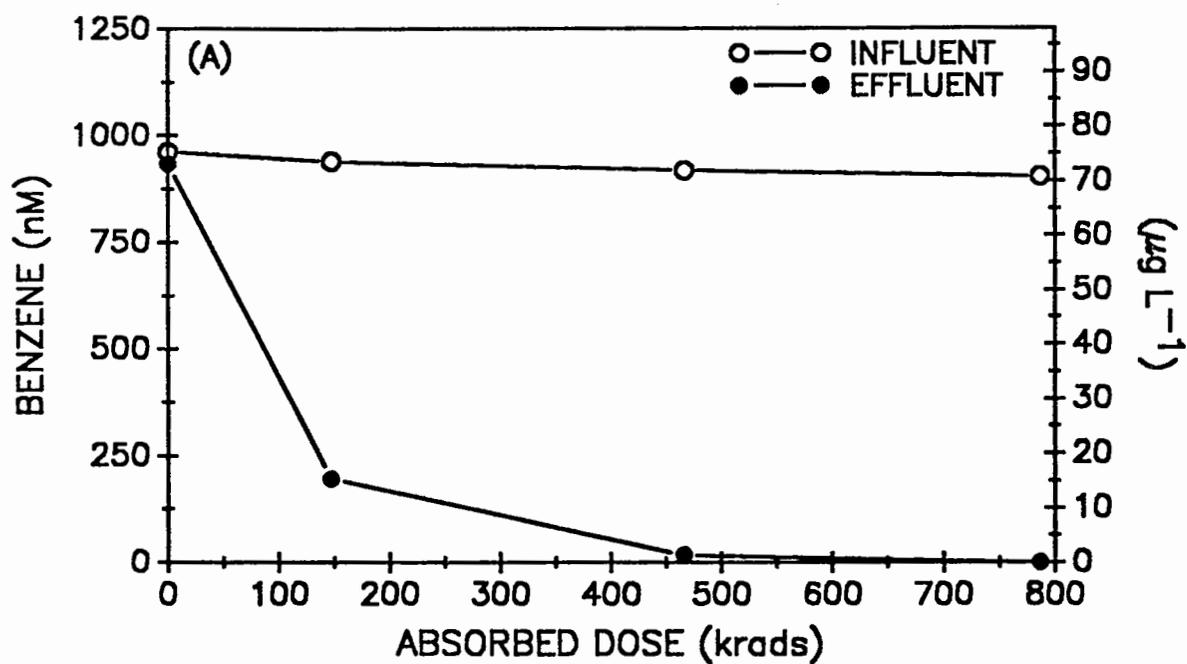


Figure 8. Removal of benzene (a) and toluene (b), at various absorbed radiation doses, from potable water.

TABLE II. SUMMARY OF SOLUTE REMOVED AND  $G_d$  FOR POTABLE WATER AND SECONDARY WASTEWATER AT TWO SOLUTE CONCENTRATIONS

Potable Water	Low Solute Concentration			High Solute Concentration		
	Dose <sup>a</sup>	[OS] <sub>d</sub> <sup>b</sup> ( $\mu$ M)	$G_d$ ( $10^3$ )	Dose <sup>a</sup>	[OS] <sub>d</sub> <sup>b</sup> ( $\mu$ M)	$G_d$ ( $10^3$ )
Benzene	155	0.74	4.6	144	8.6	57.8
	469	0.92	1.9	469	14	28.1
	797	>0.9	-	794	16	19.0
Toluene	155	0.88	5.5	144	10	68.0
	469	1.1	2.3	469	13	27.1
	797	>1.2	-	794	14	17.0
Secondary Wastewater						
Benzene	144	0.73	4.9	144	5.1	33.9
	465	0.88	1.8	469	9.0	18.7
	779	0.94	1.2	794	12	14.7
Toluene	144	0.78	5.2	144	7.8	51.8
	465	1.2	2.5	469	13	27.3
	779	1.3	1.6	794	14	17.5

<sup>a</sup>Units = krads.  
<sup>b</sup>[OS]<sub>d</sub> = organic solute concentration removed at an absorbed dose d.

The dose required to remove half of the initial benzene and toluene concentration in potable water was approximately 1.5-fold lower than the dose required to remove a similar concentration in secondary wastewater, at low solute concentration. The dose constant for benzene in secondary wastewater was higher when compared to potable water, while the dose constant for toluene was similar in both waters. The significance of the differences in  $d_{1/2}$  is not known at this time.

For the two aromatic compounds studied the OH· was the radical most responsible for the removal of the individual solute. In the case of toluene the H· could account for up to 16% of the removal. This may be significant in explaining the increased removal of toluene relative to benzene. In a natural water the observed removal efficiencies will vary because of the presence of natural radical scavengers and thus it is difficult to predict *a priori* the removal efficiency of the various organic solutes.

TABLE III. SUMMARY OF OBSERVED PSEUDO-FIRST-ORDER HIGH-ENERGY ELECTRON IRRADIATION DOSE CONSTANTS

Potable Water	Initial Concentration ( $\mu\text{M}$ )	Observed $k_{ei}$ ( $\text{krad}^{-1}$ )	$d_{1/2}$ (krad)	$r^2$
Benzene	0.934	$8.40 \times 10^{-3}$	82.5	0.99
	17.0	$3.05 \times 10^{-3}$	227	0.99
Toluene	1.15	$6.09 \times 10^{-3}$	114	0.99
	16.4	$2.22 \times 10^{-3}$	312	0.86
<b>Secondary Wastewater</b>				
Benzene	1.04	$2.63 \times 10^{-3}$	264	0.86
	16.2	$1.60 \times 10^{-3}$	433	0.99
Toluene	1.35	$3.75 \times 10^{-3}$	185	0.95
	17.1	$2.18 \times 10^{-3}$	318	0.92

Several reaction by-products have been identified in irradiated solutions of benzene and toluene. Our results are consistent with reported findings showing that phenols are an initial product in the decomposition of the compounds studied. Figure 3 shows the results of total phenol analysis, for the irradiation of an aqueous mixture of all compounds, at various doses in secondary wastewater. These results support the reported studies in that at low doses the effluent phenol concentration increases and then falls below the influent (or background) concentration at high doses. In addition to phenol, more highly oxidized species have also been observed. Glyoxal, at sub- $\mu\text{M}$  concentrations, was identified qualitatively in this study. A control experiment in which only secondary wastewater (no added organic solutes) was irradiated showed no formation of glyoxal. Several other aldehydes were observed but the structures of these compounds have not yet been determined.

### CONCLUSIONS

In conclusion, we have shown that high energy electron beam irradiation is effective in removing organic chemicals from aqueous streams. The examples shown are typical of organic chemicals found at Superfund sites. The results indicate that this process is an ultimate treatment process for the removal of toxic and hazardous organic chemicals from aqueous solutions.

Additional studies are in progress to irradiate aqueous solutions of the solutes, in similar matrices, in the absence of methanol. These results will provide better estimates of the removal efficiencies likely to be encountered in contaminated groundwaters, and it will enable a better characterization of reaction by-products.

In summary, several of the features of this process that result in its unique ability as a treatment process are that solutions that contain up to 10% solids (sludges) can be irradiated and organic compounds destroyed. And, secondly the presence of both  $e^-_{(aq)}$  and  $OH\cdot$  in aqueous solution, at similar steady state concentrations, is unique to this process and distinguishes it from other advanced oxidation processes (15). A third feature is the presence of significant concentrations of  $H\cdot$  that may react with solutes of interest and increase the efficiency of removal of some toxic organic compounds.

## TECHNOLOGY TREATMENT COST ESTIMATES

The cost of treatment using the electron beam technology depends on many factors such as the dose required to obtain the desired detoxification, the volume of waste to be treated, the size of the treatment facility, etc. For example, the cost of permanent facilities such as the one in Miami will range from \$600K to \$2,500K for 300 KeV to 3 MeV systems. Assuming the \$1,750K Miami facility at 120 gpm and a total absorbed dose of approximately 650 krads is adequate for a specific treatment application, treatment costs would be approximately \$8 per 1000 gallons if capital costs are amortized at 10% over 20 years and the facility is operated approximately 8,000 hours per year. Transportable units will undoubtedly be developed in the near future. The costs of operating such units will probably be higher due to transportation costs and increased maintenance requirements.

## ACKNOWLEDGEMENTS

All of the experimental results reported in this paper were obtained with supported by the National Science Foundation (NSF), Grant Number CES-8714640. More recently a Cooperative Agreement No. CR-816815-01-0 and a Grant No. R-816932-01-0, from the US Environmental Protection Agency have been recieved and no experimental data have been obtained as yet. The cooperation of the Miami-Dade Water and Sewer Authority was essential in the completion of the work.

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## SOIL BARRIER ALTERNATIVES

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### ABSTRACT

Manufactured clay products, cementitious materials, and soil modification processes are being marketed as landfill liners, cover systems for closed waste sites, soil berms built as secondary containment structures, and other waste management structures required to restrict liquid migration.

This paper describes currently available materials and processes. Differences in properties, construction, installation, and hydraulic performance are presented. The advantages and disadvantages of alternatives to several feet of compacted soil are discussed. Limited published information on alternative barriers is critiqued. Conclusions regarding the merits of use of alternative materials and processes in various residuals management applications are presented.

This paper has been reviewed in accordance with the U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

### INTRODUCTION

A 3-ft(0.9 m) thick layer of low-permeability, compacted soil is a required component of secondary liners for hazardous waste landfills and surface impoundments regulated under the Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) [EPA, 1985]. The recommended designs for cover systems over RCRA hazardous waste landfills and closed surface impoundments include a 60-cm thick layer of low-permeability, compacted soil [EPA, 1989]. Minimum design requirements for liner and cover systems for non-hazardous waste landfills vary from state to state, but many include a layer of low-permeability compacted soil.

Waste disposal facility owners and operators seeking RCRA permits, and responsible parties seeking designs for closure of remedial action sites are requesting approval of commercial materials and soil treatment processes as alternatives to several feet thickness of compacted soil. Alternative barrier materials possess both advantages and disadvantages in each unique application. This report summarizes the Agency's current state of knowledge and expresses technical concerns regarding the structural and hydraulic performance of available or proposed alternative barrier materials and soil modification processes.

## EQUIVALENT OR ALTERNATIVE ?

The main function of low-permeability, compacted soil is either to restrict infiltration of water into buried waste (in cover systems) or to limit seepage of leachate from the waste (in liner systems). Other objectives may include enhancement of the efficiency of an overlying drainage system, enhancement of the effectiveness of an overlying geomembrane, adsorption and attenuation of leachate, restriction of gas migration, and others. In the case of a cover system, compacted soil must also be able to withstand subsidence or differential settlement, and must be repairable if damaged by freezing, desiccation, or biologic intruders. For liner systems, the liner must be able to withstand chemical degradation from the liquids to be contained. In addition, low permeability compacted soil must have adequate shear strength to support itself on slopes and to support the weight of overlying materials or equipment.

Fundamental compositional and structural differences between compacted, low-permeability soil and alternative materials create inevitable differences in hydraulic properties, solute attenuation capacity, time of travel of chemical compounds, structural strength, desiccation resistance, freeze/thaw resistance, reaction to settlement, ease of repair, and useful life. Table 1 presents a qualitative list of factors differentiating between compacted soil and clay-blanket alternative barrier materials.

An alternative barrier material, in order to be fully equivalent to a compacted soil layer, must serve the same functions as compacted soil. Due to inherent differences in the composition and construction of compacted soil and alternative materials, the two categories of barrier structures can never be "equivalent" in all possible respects. For example, compacted soil is usually from 2 to 5 ft (0.6 to 1.5 m) thick, whereas the alternative barriers are all typically a fraction of an inch to possibly a few inches (a few mm to a few cm) in total thickness. Due to differences in thickness, an alternative barrier is bound to be more vulnerable to puncture or other damage than a much thicker layer of compacted soil.

Materials such as cements, grouts, and asphalts which are applied as viscous liquids in layers one to four inches ( 2.5 to 10 centimeters) in thickness must maintain their integrity after curing. Shrinkage cracks which develop with time must not be allowed. The problem of quality control, for example assuring consistent thickness of the applied material, has not been addressed in use of these

TABLE 1. COMPARISON OF DIFFERENCES IN ALTERNATIVE BARRIER MATERIALS

<u>Compacted Soil</u>	<u>Clay Blanket Alternative</u>
Thick (2 - 5 ft, or 0.6 - 1.5 m)	Thin ( $\leq$ 10 mm)
Field Constructed	Manufactured
Difficult to build correctly	Easy to build (Unroll & Place)
Impossible to puncture	Possible to damage or puncture
Constructed with heavy equipment	Light construction equip. used
Usually requires test fill at each site	Repeated field testing not needed
Site-specific data on soils needed	Manufactured product; data available
High leachate attenuation capacity	Low leachate attenuation capacity
Relatively long containment time	Shorter containment time
Large thickness takes up space	Little space is required
Cost is highly variable	More predictable cost
Soil has low tensile strength	Higher tensile strength
Can desiccate and crack	Can't crack until wetted
Difficult to repair	Not difficult to repair
Vulnerable to freeze/thaw damage	Probably less vulnerable to freeze/thaw damage
Performance is highly dependent upon quality of construction	Hydraulic properties are less sensitive to construction variables
Slow construction	Much faster construction

materials in waste management structures. Soil particle binders, such as numerous types of organic polymers, must be proven stable over the expected lifetime of the waste management facility. Although many of these materials, such as polyacrylamides and urethanes, have proven applicability to agricultural soil sealing, their long-term structural and hydraulic performance in waste containment or infiltration prohibition at hazardous waste sites has not been clearly demonstrated. Barrier materials created by binding mineral particles together are unlikely to possess contaminant sorption properties found in compacted soils.

Materials installed as discreet panels of impervious material suffer from lack of clear demonstration of seam integrity. Mechanical overlapping appears to be adequate with some materials, primarily bentonite blankets installed in cover systems using the "shingle" approach on sloped areas. Joint compounds and installed integrity proposed for rigid panels such as fiberglass, compressed concrete, or other materials must be demonstrated by objective studies before general acceptance can be recognized.

When the potential use of an alternative barrier is evaluated for a specific project, the critical functions of the barrier should be identified. "Equivalency" should be evaluated on the basis of the critical parameters and not necessarily upon all potential areas of comparison. Further, it must be remembered that all liner materials possess inherent advantages and

disadvantages---no single type of liner material can be considered optimum for all applications. The site-specific design function of a waste containment liner, a precipitation infiltration barrier, or a groundwater control structure, must be the basis upon which alternative barriers are compared.

## AVAILABLE MATERIALS AND PROCESSES

Currently, the marketplace is dominated by thin, manufactured, low-permeability blanket-like products containing a thin layer of bentonite clay. Other products such as spray-on concretes, grout formulas, asphalt coatings, polyacrylamide or urethane liquid formulations, resins, epoxies, latexes, and prefabricated panels have been proposed and advertised.

Clay-blanket types of materials include at least four products from different manufacturers. These are supplied as rolls and installed in a manner similar to that used for geomembranes. Seams joining adjacent sheets are achieved by overlapping by amount specified by the supplier for each product.

One of the alternative barrier materials is Bentomat(R), which consists of 1 lb/ft<sup>2</sup> (4.9 kg/m<sup>2</sup>) of bentonite sandwiched between two geotextiles that are needlepunched together. Hydraulic conductivity of small specimens permeated in the laboratory with water was found to vary with effective confining stress but is generally in the range of 10<sup>-9</sup> to 10<sup>-8</sup> cm/s for confining stresses of 8 to 12 psi (55 to 82 kPa). Practically no data are available on hydraulic properties of overlapped seams or hydraulic properties when the material is permeated with liquids other than water.

Claymax(R) consists of 1 lb/ft<sup>2</sup> (4.9 kg/m<sup>2</sup>) of bentonite sandwiched between and glued to two geotextiles. Hydraulic conductivity of small laboratory specimens was found to vary from approximately 1 x 10<sup>-8</sup> cm/s at an effective confining stress of 2 psi (14 Kpa) to 3 x 10<sup>-10</sup> cm/s at an effective confining stress of 30 psi (207 Kpa). Hydraulic conductivity to chemicals was found to vary with the chemical and to be very sensitive to whether or not the bentonite was prehydrated with water prior to introduction of the chemical. Under carefully-controlled test conditions, overlapped seams were found to self-seal, provided the minimum recommended overlap width (6 in. or 150 mm) was provided.

Gundseal consists of 1 lb/ft<sup>2</sup> (4.9 kg/m<sup>2</sup>) of bentonite glued to a 20-mil (0.5 mm) high density polyethylene (HDPE) sheet. Practically no data are available on the hydraulic conductivity of the bentonite or the shear strength of the material. Under carefully-controlled test conditions, overlapped seams were found to self-seal, even with as little as 1.5 in. (38 mm) of overlap.

Bentofix is similar to Bentomat in that bentonite is sandwiched between two geotextiles that are needlepunched together. The hydraulic conductivity of small samples of the material is reported to be approximately 1 x 10<sup>-9</sup> cm/s (testing conditions not reported). Information on other characteristics

of the material could not be located.

Gunite, shotcrete, Portland cement grouts, and similar materials have been proposed as low-permeability waste containment barriers. These are claimed to possess high density and strength, high chemical resistance, and low permeability. The desirable barrier properties are based on this industry's experience with wall coatings, reservoirs, and tanks.

Soil stabilizing reagents used in civil engineering have been proposed by many suppliers as compacted soil substitutes. These include liquid compounds used as dust palliatives, binders applied to stabilize sandy soils, erosion control chemicals, and reagents applied to control water loss from irrigated farmland in arid regions.

Hydraulic and structural performance of various other alternative materials have only been sparsely documented in published literature. Flyash-bentonite-soil mixtures show promise in terms of providing low hydraulic conductivity and high strength. Super-absorbent geotextiles, such as Fibersorb(R), have been proposed. Sprayed-on geomembranes, applied to a bentonitic blanket material, have been manufactured. Custom-made bentonite composites with geomembranes or geotextiles have been produced to meet specific customer specifications.

#### ADVANTAGES AND DISADVANTAGES OF ALTERNATIVES

Alternative barriers have been claimed to possess several economic and technical advantages over compacted soil:

- + Installation proceeds rapidly and with relative simplicity;
- + A more predictable (than with compacted soil) end-product results where quality of a compacted soil has low assurance;
- + Cost may be as much as one-tenth that of compacted soil;
- + Much less volume is required, providing 1) more landfilling space available, 2) fewer truckloads of materials needed for construction, )3 less settlement of underlying wastes because alternative materials may weigh less than thick soil;
- + Lighter construction equipment may be used, resulting in less stress on underlying geosynthetic components;
- + Retesting of material may be unnecessary after an alternative material or process is initially thoroughly characterized;
- + Unique self-repair or contaminant sorption characteristics may be beneficial where bentonite or similar components are part of the barrier.

Disadvantages include several technical deficiencies in materials and the unknown quantity of future performance due to lack of credible testing data:

- A general sparsity of objective and independent performance data;
- Limited field performance experience and data, especially long-term;
- Vulnerability to damage during construction, due to thin physical nature of materials;
- Vulnerability of sodium bentonite to adverse chemical reactions with leachate constituents;
- Unknown tolerance to settlement of underlying waste deposits;
- Unknown effects of cyclic wetting, drying, freezing, and/or thawing upon bulk shrinkage;
- Incomplete characterization of hydraulic and structural performance of overlapped seams under field conditions;
- Potential for instability when installed on slopes common in landfill structures;
- Unknown performance when overlain by a confining geomembrane which intensifies temperature differentials.

#### CONCERNS

Several major structural and hydraulic concerns require clear answers before many of these alternative materials can be proven as long-term effective pollution control barriers. These include installation quality assurance measures, slope stability, seam integrity, stability to settlement or subsidence, and resistance to climatic impacts.

Although vendors of some alternative materials have developed clear guidance regarding installation, such as permissible weather conditions, traffic protection, and seam construction and testing, others have minimal or absent guidance in these areas.

Stability of alternative barriers on slopes was the most important factor requiring sound design and performance data concluded from a Workshop conducted by the U.S.EPA [Daniel and Estornell, 1990]. The low friction angle where wet bentonite is stable prevents use on steeper slopes that landfill liner and cover designers need to provide maximum waste capacities. Attempts to increase the stable slope of bentonite blanket materials include needlepunching between the confining geofabrics, and texturing the exterior geofabric surfaces. Slope stability of thin soils stabilized with polymers, and prefabricated panels other than commonly used geomembranes has not been documented in available literature.

Changes in hydraulic performance after installation has been a significant unanswered question. Clay blankets are installed dry, with any hydration and subsequent sealing against liquid flow occurring as seepage develops and hydrates the bentonite into a low-permeability mass. Hydration of a field-installed unit by seepage of a contaminant liquid has not been examined; although numerous laboratory test data show a variety of results. The available laboratory data emphasize the need for compatibility testing similar to that required for compacted soil and geomembrane materials. A related hydraulic concern is the potential for migration of clay particles from the blanket, with possible clogging of underlying drainage management systems.

Seam integrity of alternative barrier products has been tested in laboratory studies (Daniel and Estornell, 1990). Results are varied, and in some cases conflict with manufacturers' claims. Dye seepage studies clearly show solute migration through seam overlaps. Standardized testing procedures are not yet available through standards organizations, so customers do not have uniform acceptability guidance.

Barriers composed of both clay and geofabric components may possess adequate strength and flexibility to tolerate moderate amounts of settlement or subsidence of underlying material. This is a significant factor in closure and cover design for landfills which may contain bio-decomposable materials. The tensile strength of these products is readily measured by laboratory techniques, but the actual stresses seen after field installation has been poorly documented. Design guidance by manufacturers to provide installation which will provide continuing conformance and hydraulic integrity with a settling foundation is not available.

Liners and cover systems for waste management structures in dry climates suffer from a greater paucity of performance data than those in humid regions. Data from computer modelling suggests that desiccation of soil compacted wet of optimum clearly is a long-term problem in dry climates. Unpublished observations show that temperature cycling during normal seasons in humid climates also causes moisture migration from compacted soils. Since alternative barrier materials are composed of much thinner materials, it may be expected that changes in structural and hydraulic characteristics may be much more drastic with climatic changes. This effect has not been documented for field installations of any of the proposed or installed alternative barrier materials. Wetting, drying, heating, or freezing of only parts of a barrier installation are also of concern. Such events may clearly require different designs or materials for north and south facing slopes of cover systems.

The resistance of all of the alternative barrier materials to biologic intruders---plant roots and burrowing animals---has not been demonstrated. These and other concerns exemplify the young stage of objective data gathering from which alternative barriers suffer.

## VIABLE APPLICATIONS OF ALTERNATIVE MATERIALS

An early reported use of clay-blanket alternative barrier material was as a backup for geomembranes in a double-composite liner system for a hazardous waste landfill designed to meet EPA's Subtitle C regulations (Schubert, 1987).

Alternative materials can serve as economic yet viable barriers when incorporated into temporary caps for some type of RCRA or CERCLA sites where settlement is expected which would damage a final cover. Although the alternative barrier may be easy to repair, it is possible that unanticipated practical problems may arise.

Alternative barriers may be less vulnerable to damage from desiccation after installation because they are installed dry. Giving stronger consideration to bentonite-rich alternatives in arid regions may be problematic when short-duration infiltration events cause sudden hydration followed by extended desiccation. Bulk shrinkage upon extended drying has not been investigated in large-area liner installations.

Landfill covers on relatively flat surfaces, free from expected subsidence, are among the least controversial applications. A well-designed and operative lateral drainage layer overlying the barrier increases confidence that the alternative construction will keep infiltration out of underlying wastes. Monitoring devices, such as large collection lysimeters, increase assurance that the barrier structures are operating according to design.

## CONCLUSIONS

Numerous alternative materials and installation processes are in the marketplace to replace several feet of compacted soil. While clear economic incentives exist to consider most of these, trustworthy performance data are sparse, and need to be individually interpreted.

Slope stability, shear strength, and interfacial friction represent the data gaps most needed to be filled in order for many alternative materials to be installed with a high level of confidence in their ultimate performance.

Hydraulic properties are readily tested with adapted laboratory procedures, but questions remain about field performance and seam integrity. The capacity and value of solute attenuation in bentonite-rich alternative barriers has not been defined.

Environmental (climatic) impacts are nearly all undocumented. These include freeze/thaw resistance, desiccation resistance, effects of settlement, claimed self-healing capabilities, and impacts of rough bedding materials.

The useful life of these materials is unknown because of their relatively recent appearance in the marketplace. Some materials possess both mineral and synthetic polymer components within one product, leading to claims about the best features of each. Whether such compositions lead to synergistic environmental barrier properties, or whether these may ultimately be antagonistic is unknown. Science and the user industry have a strong need for all experiences with alternative barrier installations to be objectively reported.

Economic incentives, installation simplicity, structural consistency of manufactured materials, and utility in geometrically complex waste management structures point to a high potential value of alternative barrier materials. With the completion of research studies currently underway, and further publication of case study data by the user industry, both regulatory agencies and waste management engineers will have a higher degree of confidence in alternative barrier performance.

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WASTE MINIMIZATION ASSESSMENT CENTERS  
COST SAVINGS RECOMMENDED AND IMPLEMENTED IN  
TWELVE MANUFACTURING PLANTS

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ABSTRACT

The Waste Minimization Assessment Center (WMAC) program was begun in 1988 under agreement with the Risk Reduction Engineering Laboratory of the U.S. Environmental Protection Agency. University City Science Center (Philadelphia, PA) manages the program through which Waste Minimization Assessment Centers assist small and medium-size manufacturers who want to minimize their formation of waste but who lack the in-house expertise to do so. Currently three WMACs at Colorado State University, the University of Louisville, and the University of Tennessee participate in the program.

Each WMAC is staffed by engineering faculty and students who have considerable direct experience with process operations in manufacturing plants and who also have the knowledge and skills needed to minimize hazardous waste generation. The waste minimization assessments, which are conducted at no out-of-pocket cost to the client, require several site-visits for each client served. The WMAC staff locate the sources of waste in each plant and identify the current disposal or treatment methods and their associated costs. They then identify and analyze a variety of ways to reduce or eliminate the waste. Specific measures to achieve that goal are recommended and the essential supporting technological and economic information is developed. Finally, a confidential report which details the WMAC's findings and recommendations including cost savings, implementation costs, and payback times is prepared for each client manufacturer.

This presentation will discuss the cost savings recommended and implemented in the 12 manufacturing plants served during the first program period of this project by the Colorado State University and University of Tennessee WMACs.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

WASTE MINIMIZATION ASSESSMENT CENTERS  
COST SAVINGS RECOMMENDED AND IMPLEMENTED  
IN TWELVE MANUFACTURING PLANTS

INTRODUCTION

The amount of industrial waste generated by industrial plants has become an increasingly costly problem for manufacturers and an additional stress on the environment. One solution to the problem of industrial waste is to reduce or eliminate the waste at its source.

To take the first practical, effective steps toward that objective, many manufacturers need help which is not available within their plants. However, that help can cost money, and it may not be as truly impartial and disinterested as the manufacturer would like it to be. Unless some practical, effective actions are taken, the problem can only get worse.

University City Science Center (Philadelphia, Pennsylvania) has begun a pilot project to assist small and medium-size manufacturers who want to minimize their formation of waste but who lack the in-house expertise to do so. Under agreement with the Risk Reduction Engineering Laboratory of the U.S. Environmental Protection Agency, the Science Center's Industrial Technology and Energy Management (ITEM) division in 1988 established two waste minimization assessment centers (WMACs) at Colorado State University in Fort Collins and at the University of Tennessee in Knoxville. A third was recently initiated at the University of Louisville.

Assessments are carried out by teams of university engineering faculty assisted by students, who seek out interested manufacturers and arrange visits to their plants to gather detailed information on waste generation and manufacturing operations. Then the university assessment team analyzes the data and other information obtained, re-visits the plant for verification and further insight, develops specific quantified recommendations (waste minimization opportunities or WMOs), and calculates their cost-effectiveness before reporting them to the manufacturers. The WMACs that performed the assessments discussed here are located at Colorado State University and the University of Tennessee.

The potential benefits of the pilot project include minimization of the amount of waste generated by manufacturers, reduced waste treatment and disposal costs for participating plants, valuable experience for graduate and undergraduate students who participate in the program, and a cleaner environment without more regulations and higher costs for manufacturers.

This publication presents a detailed account of the recommendations offered to and implemented by the first 12 manufacturers served by the WMACs at Tennessee and Colorado State. To obtain this information, professional staff members from these WMACs contacted the manufacturers to learn the outcome of every recommendation that had been offered -- specifically whether it was implemented, when, and what the plant's experience had been with costs, savings, and waste reduction.

An analysis of the financial benefits of implementation is offered for all 12 manufacturers as a group and for the federal government, which can derive revenue by taxing the manufacturers' cost savings as incremental income.

## SUMMARY OF PLANTS AND ASSESSMENT RESULTS

According to Table 1 these twelve plants were spending a total of \$1.05 million/year on waste management before the WMACs assessed their operations and identified waste minimization opportunities (WMOs). In aggregate, the net cost savings recommended amount to almost \$1.3 million/year. Including savings in raw material costs enables the total cost saving to be larger than the cost of waste management.

The cost-saving approach taken with these results is generally conservative, because the WMOs address only the avoidance of raw materials costs and the reduction of present and future costs associated with waste treatment and disposal. Not claimed are the savings related to: possibly stricter emission standards, any liability incurred from waste management practices, and costs arising from employe health and safety problems.

There are some common characteristics found in these plants' operations, the wastes which they generate, and the WMOs recommended to reduce the quantity and the cost of waste management. We have utilized these commonalities to place the results from the 12 plants into these five descriptive (but somewhat arbitrary) categories of cost-saving WMOs:

- I. Substitution of Plant Operation or Material
- II. Changes in Technique or Control Method
- III. Reduction of Solvent Use
- IV. Reduction of Liquid Volumes
- V. Reduction and Treatment of Sludge

The shares of cost savings attributable to each of these categories are shown in this tabulation:

Category	Net Savings Value (\$/yr minimum)	Share (%)
I.	570,299	46.2
II.	410,443	33.2
III.	187,510	15.2
IV.	62,429	5.0
V.	4,804	0.4
Total	1,235,485	100.0

This total is slightly smaller than that shown in Table 1 because some options have been deleted here to give a more conservative count. If two or more optional recommendations were given to a manufacturer, the smaller savings options were excluded from this total.

It is obvious that substitution of a plant operation or a material (Category I) accounts for about 46% of the total savings found. When that share is combined with changes in technique or method of process control (Category II), almost 80% of the savings can be accounted for. This statistic clearly indicates the kind of WMO to be sought in trying to reduce the costs of waste to small and medium-size manufacturers. It is more significant because of the wide variety of plants included among the 12 plants served by the WMACs.

Reduction of solvent use (Category III) is responsible for about 15% of the net cost savings found among the twelve plants. This category includes not only solvent recovery and recycle but also taking measures such as better control of solvent use to prevent its loss.

## IMPLEMENTATION OF WMACs' RECOMMENDATIONS

Implementation results for each of the 12 manufacturers served by a WMAC during the 1988-89 program period are summarized in Tables 2A and 2B. Collectively they show:

- Forty-five of the 87 waste minimization opportunities (WMOs) recommended have been implemented or definitely will be within two years (not later than 1991). That represents a 52% implementation rate for WMOs related to waste management or raw material savings. (If a WMO produced savings in waste management and raw material costs, the WMO was treated as two recommendations, either or both of which could be implemented.)
- Total implemented savings for the manufacturers are \$685,855/year, which represents 49% of all the cost savings recommended by the WMACs.
- When examined separately, WMOs which produce waste management savings are being implemented at a higher rate (66.5%) than those which produce raw material savings (38.8%).

Implementation statistics can be affected dramatically by a few recommendations. Table 2A reveals that decisions by Tennessee manufacturers not to implement four WMOs had a relatively large impact upon overall results. If they had been implemented, raw material savings would have roughly doubled to \$706,000/year, which then would have raised the implementation rate to more than 80% for this savings category.

The implementation rates found among the 12 manufacturers are consistent with the previously reported results of in-person interviews with representatives of these plants. Eleven of the 12 said that the WMAC's assessment had led to waste reduction and dollar savings or was expected to. There is a variety of reasons given in Tables 2A and 2B for not implementing specific WMOs. All together, 26 WMOs were rejected, and the most common reason given is that the WMO involves an unacceptable operating change to the plant (9 times). In only three instances was the recommendation considered impractical, but in six instances the WMO was considered unnecessary because the plant had, in the meanwhile, changed its operating practices.

The twelve plants do not offer a large enough sample to draw broad conclusions about industries (SIC codes) and the types of recommendations being implemented. As more plants are served and their implementation data become available, conclusions of that kind will be more justifiable than they are at the present time.

## FINANCIAL ANALYSES OF WMOs IMPLEMENTED

Profitability and rate of return are the kinds of financial analyses applied to the implemented waste minimization opportunities reported by the WMACs from the first twelve assessments made of small and medium-size manufacturing plants.

The internal rate of return (IRR) is calculated from the following standard equation:

$$0 = CF_0 + \{CF_1/(1+i)\} + \{CF_2/(1+i)^2\} + \dots + \{CF_n/(1+i)^n\}$$

in which            CF = cash flow  
                          CF<sub>subscript</sub> = the year in which the cash flow occurs  
                          i = IRR

It is based upon a series of cash flows (usually annual) and, by inserting the cash flow data, the user is able to calculate a value for  $j$ , which is the internal rate of return. The initial investment, represented by  $CF_0$ , is negative because it represents an outflow of money. Earnings, on the other hand, are positive, and that mathematical convention is observed when the individual cash flows are inserted into this equation. In effect, IRR is the rate of return at which the sum of discounted sequential cash flows equals the initial investment.

Another way of interpreting IRR is to say that it is the value by which a series of cash flows is to be discounted, in the manner prescribed by this equation, so that their algebraic sum is equal to the initial investment. Obviously, when IRR is large, the initial investment is considered to be more profitable.

Profitability is reported here as a profitability index, which is derived by first calculating the net present value of the same series of annual cash flows discounted at a specified rate (usually 10, 15, or 20%), instead of the IRR. This equation can be expressed in the following manner:

$$NPV = CF_0 + \{CF_1/(1+DR)\} + \{CF_2/(1+DR)^2\} + \dots + \{CF_n/(1+DR)^n\}$$

in which            NPV = net present value  
                            $CF_{\text{subscript}}$  = cash flow for a specific year  
                           DR = discount rate specified

The profitability index (also known as leverage ratio) is the ratio of the net present value, calculated according to this equation from a series of cash flows, to total capital investment needed to implement the WMOs.

It is clear from Tables 2A and 2B that WMOs are implemented in various years rather than all at once. The net cash flow for a given year is calculated under the following conditions:

- All costs are capitalized.
- All investments are depreciated linearly over 5 years to a net value of zero.
- All funds needed for implementation are borrowed at a specific rate, and loans are amortized in equal annual payments over 5 years.
- Manufacturers' savings are taxed as incremental income at a rate of 25%.
- Savings from a specific capital investment do not begin until the year after the investment is first made. (Thus, the initial net cash flow is always negative and it diminishes manufacturers' tax liability at the 25% rate.)
- Implementation costs and the savings they produce increase at a constant rate, which must be chosen for each case.

As expected, lower borrowing rates are beneficial to the federal government's returns from its investment in the WMAC program and to manufacturers' profitability as a result of implementing waste minimization opportunities recommended by the WMACs (Table 3). However, investments in WMOs are still very attractive even at borrowing rates of 15%. For example, at a 15% rate manufacturers as a group earn \$2.18 within five years for every dollar invested in a recommended waste minimization opportunity (10% discount rate assumed on cash flows). If the borrowing rate is 9%, this earning figure goes up to \$2.81. The federal government's financial returns are \$2.85 at a manufacturers' 15% borrowing rate and \$3.08 at a 9%

rate. Internal rate of return follows a similar direction, but very large values of IRR (434 to 660%) are difficult to interpret as measurements of profitability.

All but one of the financial analyses reported here were made with the assumption that implementations costs and the savings in waste management and raw materials which they produce increase at 6% per year. For example, an initial capital investment made in 1990 would then cost 6% more than it did when its size was calculated in 1989, and the savings realized would also be 6% larger. The one exception was calculated at a 3% rate, and the effects are shown in Table 4. It is clear that WMO investments made with larger rates of increase in costs become even more profitable if savings in waste management and raw materials increase at the same rate.

Risk is always a deterrent to action, and manufactures naturally hesitate to make capital investments until they are confident about the outcome. The timing of implementation expenditures used in this report is whatever the manufacturers stated during the WMACs' collection of implementation data. On a hypothetical basis, a financial analysis was made by assuming that the manufacturers' second- and third-year implementations were accelerated by a year. The results in Table 5 reveal even better profitability for the federal government and the manufacturers for accelerated investments.

The policy implications of these two sets of calculations are these:

- A faster rate of cost increases does not harm profitability and, in fact, enhances profitability if savings increase at the same rate.
- Accelerating the rate of expenditures to implement WMOs makes the investments even more profitable, and incentives which accelerate the rate can be justified by the improved financial returns.

The financial analyses of implemented WMACs' recommendations demonstrate rather convincingly that investments in waste reduction are good for the manufacturers, for the federal government, and eventually for the environment.

TABLE 1. SUMMARY OF PLANTS SERVED BY WMAC PROGRAM

Plant No.	SIC Code	Principal Product	Cost of Waste Mgmt. (\$/yr)	Net Cost Savings (\$/yr)*
1	2759	Commercial Printing	53,540	145,750
2	2851	Paints, Varnishes, and Allied Products	88,860	22,110
3	3411	Metal Cans	249,850	133,060
4	3443	Fabricated Plate Work	99,510	337,870
5	3471	Plating, Polishing, Anodizing Parts	14,910	9,438
6	3479	Coating, Engraving, and Allied Services	35,250	234,880
7	3585	Air-Conditioning, Air-Handling, Refrigeration Equipment	147,940	217,135
8	3672	Printed Circuit Boards	86,848	42,225
9	3672	Printed Circuit Boards	32,609	14,080
10	3743	Railroad Equipment	142,970	42,427
11	3823	Industrial Measuring Instruments	35,940	12,510
12	3993	Signs and Advertising Specialties	61,210	62,210
		Totals	1,049,437	1,273,695
		Means	87,453	106,141

\*This figure includes savings in raw materials costs as well as waste management costs.

TABLE 2A  
SUMMARY OF IMPLEMENTED AND RECOMMENDED WASTE MINIMIZATION OPPORTUNITIES  
1988-89 WHAC PROGRAM

UNIVERSITY OF TENNESSEE

Report No.	SIC Code	Brief WMO Description	Impl. Date	Waste Mgt. Savings Recommended (\$/yr)	Waste Mgt. Savings Implemented (\$/yr)	Raw Material Savings Recommended (\$/yr)	Raw Material Savings Implemented (\$/yr)	Impl. Cost (\$)	Reason for Not Implementing.	
452	42-1	3479	Reduce peak solvent concentration.	1988	0	----	4,995	4,995	12,400	
			Reduce primer surface area.	----	0	----	11,238	----	3,000	Unacceptable operating change.
			Reduce primer partial pressure.	1991	0	----	2,997	2,997	2,900	
			Minimize product rejection.	----	8,247	----	200,711	----	28,000	Rework process now done offsite.
			Use physical stripping.	----	<u>10,410</u>	----	<u>46,241</u>	<u>----</u>	150,000	Rework process now done offsite.
				18,657	0(0%)	266,182	7,992(3%)	196,300		
42-2	3993	Electrostatic spray system.	----	14,022	----	11,566	----	4,400	Unacceptable operating change.	
		Improve spray equipment.	1990	4,674	4,674	3,855	3,855	6,000		
		Re-train spray personnel.	1989	1,870	1,870	1,542	1,542	3,000		
		Minimize residual paint.	----	4,816	----	6,767	----	700	Unacceptable operating change.	
		Install screen cleaning booth.	----	0	----	10,824	----	22,880	Impractical.	
		Use template for letter fixation.	1990	0	----	1,980	1,980	195		
		Use adhesive tape for letters.	----	0	----	1,980	----	100	Impractical.	
			1989	<u>0</u>	<u>----</u>	<u>5,260</u>	<u>5,260</u>	<u>1,500</u>		
				25,382	6,544(26%)	43,774	12,637(29%)	38,775		

TABLE 2A, cont'd.  
UNIVERSITY OF TENNESSEE

Report No.	SIC Code	Brief WMO Description	Impl. Date	Waste Mgt. Savings Recommended (\$/yr)	Waste Mgt. Savings Implemented (\$/yr)	Raw Material Savings Recommended (\$/yr)	Raw Material Savings Implemented (\$/yr)	Impl. Cost (\$)	Reason for Not Implementing.	
42-3	3743	Reduce generation of paint chips.	1990	14,334	14,334	10,651	10,651	13,500		
		Electrostatic spray system.	----	5,431	----	7,647	----	58,320	Too expensive initially.	
		Re-train spray personnel.	1990	1,843	1,843	2,977	2,977	3,500		
		Minimize overspray.	1989	<u>1,843</u>	<u>1,843</u>	<u>300</u>	<u>300</u>	<u>0</u>		
				23,451	18,020(77%)	21,575	13,928(65%)	75,320		
453	42-4	3443	Cover degreaser tank.	----	0	----	17,182	----	220	Unacceptable operating change.
			Reduce oil pick-up.	----	930	----	79	----	290	Impractical.
			Install ultrasonic cleaner.	1991	3,075	3,075	17,376	17,376	50,000	
			Minimize salt carry-over.	----	6,000	----	16,128	----	43,800	Switching to a new system.
			Use vacuum brazing.	1990	22,800	22,800	180,643	180,643	720,640	
			Reduce paint carry-over.	1989	2,996	2,996	1,351	1,351	2,790	
			Electrostatic paint	----	5,414	----	5,789	----	13,200	Installing new system.
			Discontinue painting.	----	<u>6,743</u>	----	<u>52,980</u>	----	<u>28,440</u>	Unacceptable operating change.
				47,958	28,871(60%)	291,528	199,370(68%)	859,380		

TABLE 2A. cont'd.  
UNIVERSITY OF TENNESSEE

Report No.	SIC Code	Brief WMO Description	Impl. Date	Waste Mgt. Savings Recommended (\$/yr)	Waste Mgt. Savings Implemented (\$/yr)	Raw Material Savings Recommended (\$/yr)	Raw Material Savings Implemented (\$/yr)	Impl. Cost (\$)	Reason for Not Implementing.
454	3585	Alternate fastening.	1989	39,520	39,520	29,330	29,330	6,400	
		Eliminate solvent adhesives.	1989	27,750	27,750	-2,060	-2,060	31,740	
		Modify adhesive usage.	----	28,427	----	-1,854	----	5,100	Solvent adhesive no longer used.
		Re-train spray personnel	----	3,619	----	5,191	----	3,500	Plant now uses prepainted parts.
		Minimize paint mist loss.	----	18,094	----	26,820	----	2,100	Plant now uses prepainted parts.
		Reduce oil loss.	1990	<u>0</u>	----	<u>56,250</u>	<u>56,250</u>	<u>6,900</u>	
				117,410	67,270(57%)	113,677	83,520(73%)	55,740	
42-6	2759	Recover solvent.	----	0	----	70,338	----	63,760	Too expensive initially.
		Auto. mixing.	----	<u>32,765</u>	----	<u>43,170</u>	----	<u>27,880</u>	Switching to new adhesive.
				32,765	0(0%)	113,508	0(0%)	91,640	

TABLE 2B  
SUMMARY OF IMPLEMENTED AND RECOMMENDED WASTE MINIMIZATION OPPORTUNITIES  
1988-89 WMAC PROGRAM

COLORADO STATE UNIVERSITY

Report No	SIC Code	Brief WMO Description	Impl. Date	Waste Mgt. Savings Recommended (\$/yr)	Waste Mgt. Savings Implemented (\$/yr)	Raw Material Savings Recommended \$/yr)	Raw Material Savings Implemented (\$/yr)	Impl. Cost (\$)	Reason for Not Implementing
56-1	3471	Recycle H <sub>2</sub> O.	----	3,625	----	0	----	4,500	Reduced H <sub>2</sub> O consumption
		Dewater sludge.	1989	2,914	2,914	0	----	15,000*	
		Reduce rinse volume.	1989	<u>1,039</u>	<u>1,039</u>	0	----	<u>10</u>	
				7,578	3,953(52%)	0	----	19,510	
455 56-2	3672	Reuse MEMTEK effluent.	----	1,554	----	1,966	----	22,000	Water quality problems
		Install filter.	1990	1,540	1,540	150	150	810	
		Reduce H <sub>2</sub> O usage.	1989	5,483	5,483	357	35	200*	
		Segregate acid soap waste.	1989	23,470	23,470	0	----	300*	
		Dewater Sn stripper.	----	3,920	----	0	----	4,500	Unacceptable operating change.
		Use more DI H <sub>2</sub> O.	----	7,090	----	0	----	9,800	Too expensive initially.
		Recycle CuSO <sub>4</sub> .	1989	280	400	0	----	0	
		Install drip bars.	----	<u>0</u>	----	<u>460</u>	----	<u>1,200</u>	Unacceptable operating change.
				43,337	30,893(71%)	2,933	507(17%)	38,810	

TABLE 28, cont'd.  
 COLORADO STATE UNIVERSITY

Report No	SIC Code	Brief WMO Description	Impl. Date	Waste Mgt. Savings Recommended (\$/yr)	Waste Mgt. Savings Implemented (\$/yr)	Raw Material Savings Recommended \$/yr	Raw Material Savings Implemented (\$/yr)	Impl. Cost (\$)	Reason for Not Implementing
56-1	3471	Recycle H <sub>2</sub> O.	----	3,625	----	0	----	4,500	Reduced H <sub>2</sub> O consumption
456	3672	Reuse effluent.	1991	1,550	1,550	5,680	5,680	13,000	
		Reduce H <sub>2</sub> O usage.	1989	0	----	2,670	2,670	250	
		Dewater spent reagents.	----	1,790	----	0	----	4,500	Space limitation
		Recycle Cu waste.	1989	1,090	1,090	0	----	0	
		Reuse rinse H <sub>2</sub> O.	1991	0	----	1,270	1,270	650	
		Install drip bars.	1991	0	----	370	370	480	
						4,430	2,640(60%)	9,990	9,990(100%)
56-4	2851	Pipe-cleaning system.	1991	3,100	3,100	8,010	8,010	1,600	
		Recover solvent.	1990	2,846	2,846	2,574	2,574	17,000*	
		Eliminate Hg additive.	1990	5,580	5,580	0	----	0	
				11,526	11,526(100%)	10,584	10,584(100%)	18,600	
56-5	3823	Use Cr-free coating.	----	5,480	----	0	----	0	Unacceptable operating change.
		Segregate waste oil.	----	6,820	----	0	----	2,500	Segregated using different method.
		Increase drain time.	1989	0	----	210	210	0	
				12,300	0(%)	210	210(100%)	2,500	
56-6	3411	Use non-hazardous wash.	1989	177,400	177,400(100%)	0	-----	0	

\*Manufacturer's estimate

TABLE 3  
EFFECTS OF BORROWING RATE ON PROFITABILITY FROM  
IMPLEMENTING WASTE MINIMIZATION OPPORTUNITIES

Borrowing Rate	Federal Government			Manufacturers		
	LR <sub>10</sub> *	LR <sub>15</sub>	IRR	LR <sub>10</sub> *	LR <sub>15</sub>	IRR
9%	3.08	2.33	54.8	2.31	1.88	660
12%	2.96	2.23	52.4	2.24	1.83	533
15%	2.85	2.12	50.1	2.18	1.77	434

\* LR<sub>10</sub> (LR<sub>15</sub>) = Leverage ratio for five-year cash flows discounted at the stated per cent (10 or 15) to the initial time period and compared to the program investment by the federal government and the capital investment by the manufacturers.

IRR = Internal rate of return.

TABLE 4  
EFFECTS OF GROWTH IN COSTS ON PROFITABILITY FROM  
IMPLEMENTING WASTE MINIMIZATION OPPORTUNITIES

Growth Rates		Returns to Federal Government			Returns to Manufacturers		
WM & RM* Costs, %	Implementation Costs, %	LR <sub>10</sub> **	LR <sub>15</sub>	IRR	LR <sub>10</sub> **	LR <sub>15</sub>	IRR
6	6	2.96	2.23	52.4	2.24	1.83	533
3	3	1.81	1.34	44.0	1.93	1.57	509

Returns are calculated at a 12% borrowing rate after taxes at 25% have been levied against manufacturers' cost savings.

\* WM = Waste Management  
RM = Raw Material

\*\* LR<sub>10</sub>(LR<sub>15</sub>) = Leverage ratio for five-year cash flows discounted at the stated per cent (10 or 15) to the initial time period and compared to the program investment by the federal government and the capital investment by the manufacturers.

IRR = Internal rate of return.

TABLE 5  
ACCELERATED VERSUS NORMAL IMPLEMENTATION

FINANCIAL CRITERION	IMPLEMENTATION SCHEDULE			
	Normal *		Accelerated **	
	Federal Govt.	Manufacturers	Federal Govt.	Manufacturers
Leverage Ratio				
10% discount	2.96	2.24	3.41	2.50
15% discount	2.23	1.83	2.60	2.04
Internal Rate of Return, IRR	52.4	533	55.1	171

\* Normal implementation occurs at the actual rate stated by manufacturers between 1989 and 1991.

\*\* Accelerated implementation occurs at a hypothetical rate between 1989 and 1990; that is, during two years rather than three.

Conditions of implementation:

- All costs are capitalized.
- All investments are depreciated linearly over 5 years to a net value of zero.
- All implementation funds are borrowed at a 12% rate and loans are amortized in equal annual payments over 5 years.
- Manufacturers' savings are taxed as incremental income at a rate of 25%.
- Implementation costs and the savings produced increase at 6%/year.

EVALUATING FINAL COVERS FOR HAZARDOUS WASTE LANDFILLS  
USING A RULE-BASED KNOWLEDGE SYSTEM

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ABSTRACT

This paper examines the use of a rule-based knowledge system for the evaluation of final covers used to close hazardous waste landfills. Following a brief discussion of final cover design and associated performance standards, a rule-based expert system which has been developed to interpret these standards is described. The goal structure, control structure, and other basic data structures used to implement the system are discussed. Specific examples of rules are presented within the context of discussion of the relationships between rules and control processes.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## FINAL COVER DESIGN

In a typical landfill used for hazardous waste disposal, pits (cells) are excavated in native soil or rock of low permeability to depths of 15 to 50 feet with the base of the cell above the water table. The practice of multi-cell construction often makes use of groups of cells separated by berms, liners and covers. A landfill under separate cover may range in size from 1 to several dozen acres. Several such landfills, collectively enclosing hundreds of acres, may comprise a single facility. Cells are commonly lined with single or multiple soil and synthetic barriers of low permeability to water ( $10^{-7}$  to  $10^{-8}$  cm/sec), and are equipped with leachate collection and monitoring systems.

A variety of wastes may be accepted at a hazardous waste landfill. Wastes may be placed in fills as bulk material, be treated with solidification agents, or be placed in drums prior to burial. Current regulations prohibit the placement of free liquids in landfills, although liquids inevitably enter the unit from precipitation and run-on that occurs during filling. Older landfills often contain wastes with relatively high liquid volumes.

Covers (or caps) are an essential feature of landfill closure. These structures serve to minimize threats to the public health and the environment which are posed by the potential or actual release of hazardous materials from the facility. Covers prevent rainwater from infiltrating into the unit and thus minimize the likelihood of leachate formation. A cover will also prevent gases and leachate from exiting the top of the fill.

A typical landfill cover consists of a multi-layer design. The top layer consists of a vegetative or armored surface underlain by several feet of topsoil. Its purpose is to minimize erosion and promote surface runoff from the cover. Below this lies a permeable soil drainage layer for removal of water which infiltrates through the top layer. Either natural soil or geosynthetic materials are used in the drainage layer. The bottom of the cover is a low-permeability layer designed to limit liquid infiltration into the underlying wastes. The recommended low-permeability layer design consists of two components: a flexible membrane liner (FML) of at least 20-mil thickness, and a compacted clay layer at least 60-cm thick with a permeability less than  $10^{-7}$  cm/sec.

Covers may include several additional layers. Filter layers, made either from natural soil or geosynthetic material, can be placed between soil layers of differing grain size distributions. Filters prevent piping of soil between the layers and help to maintain layer integrity over time. A biotic barrier may also be included in the structure to prevent plant roots and burrowing animals from disturbing the drainage and low-permeability layers. A barrier layer typically consists of either tightly packed cobbles or a thin polymeric material releasing a herbicide at a controlled rate. Lastly, a gas vent layer is often included to collect and transport landfill gases to a collection point where they can be safely

treated or disposed. Perforated vertical collector pipes penetrating to the bottom of the landfill may be used as vents in conjunction with the gas collection layer.

Under the Resource Conservation and Recovery Act (RCRA) of 1976, performance standards for hazardous waste landfill covers have been published in the Code of Federal Regulations (40 CFR 264.310). These regulations require that the final cover be designed and constructed to:

- 1) accommodate settling and subsidence in order to maintain the structural integrity of the cover,
- 2) minimize erosion or abrasion of the cover,
- 3) promote drainage of surface and infiltrated water from the cover,
- 4) minimize migration of fluids through the landfill to ground and surface waters,
- 5) have a permeability no greater than that of the landfill's bottom liner system or of the natural soils present, and
- 6) function with minimum maintenance over the post-closure period.

Regulatory agencies responsible for reviewing applications for permits to operate or close hazardous waste landfills must ensure that final cover designs submitted by the owner/operator will satisfy these criteria. Since regulatory standards are based on cover performance and not design characteristics, application of these standards at the time of design often poses special problems.

Construction of a cover system which will last for a number of years with minimal maintenance requirements depends on the use of sound engineering practices derived from particular knowledge which has been accumulated over time. Much of the knowledge needed for cover evaluation also involves concepts that have been refined through practical design experience. Properties of buried wastes, the materials and methods used to construct the cover, and the effects of interactions between various cover materials and the waste or its by-products, must be evaluated.

An expert system named F-Cover, which encodes guidelines for cover design, is currently being developed. An initial version of this system has been released for evaluation and testing. It is anticipated that F-Cover will be particularly useful in assisting the permit review process of evaluating landfill cover performance standards.

#### KNOWLEDGE REPRESENTATION

In operation, the F-Cover system first requests that the user provides a layer design sequence for the proposed cover. The user also

provides information about materials to be used, layer thicknesses, permeabilities, and other basic data. The system uses this data and internal information to generate questions for the user. Responses in turn are used to determine other properties and characteristics of the cover design. As required information is supplied through this interview process, the system incrementally assembles conclusions by 'reasoning' about the data. Eventually, the system determines that sufficient information has been provided to determine final conclusions regarding the adequacy of the design. A text report is output for review after the interview and all evaluation processes have been completed.

The knowledge sources used to develop F-Cover include published design manuals, proposed EPA guidelines, and experts from the EPA and private consulting firms. Given the way in which cover performance standards are stated, it is natural to express design knowledge and conditions through which regulatory objectives are satisfied in the form of rules.

Indeed, it is possible to express the basic operation of the cover review process in a single rule: Abstracted from the system, this rule can be stated as follows:

```
IF    subsidence potential has been accommodated
AND   erosion potential has been minimized
AND   liquid migration is minimized
AND   the drainage system is adequate
AND   the cover meets permeability regulations
AND   maintenance is minimized
THEN  the cover design is approved
ELSE  the cover design is (or may be) insufficient.
```

This rule corresponds to the top-level of the goal tree diagram shown in Figure 1. Also, the conditions expressed in this rule's premise correspond directly to the six performance standards listed in the previous section. (See the Appendix for a more detailed explanation of the rule syntax used in this chapter.)

Although the concept expressed by this rule is represented in a slightly different manner in the F-Cover system, the underlying logic of the system is essentially the same. In F-Cover, conditions expressed in the top-level rule premises are represented by data objects (variables), and each such variable is evaluated to determine whether or not the cover design is approved. Additional rules are used to evaluate each condition. Proceeding in a logical order through the knowledge domain, toward more specific design parameters, the third premise in the main rule can be considered as an example. This premise, "minimization of erosion potential" is expanded through a rule such as the following:

```
IF    no erosion deficiencies are found
THEN  erosion potential is minimized
```

ELSE erosion potential is not minimized  
 OR erosion potential is unknown.

In other words, if the rule base has been evaluated for all erosion-related deficiencies and none were found, then erosion potential has been minimized. Conversely, if a substantive erosion deficiency or certain information about erosion potential is missing, it is concluded that either erosion potential cannot be assessed from the information provided, or a potential erosion problem exists. The first conclusion is reached if calculations of the rate of erosion from the cover have not been supplied and no other deficiencies are found. The second conclusion is satisfied when any condition determines that an unacceptable rate of erosion is likely (i.e., at least one substantive deficiency is detected). Through similar processes, all higher-level goals are assigned values as a function of lower-level processing.

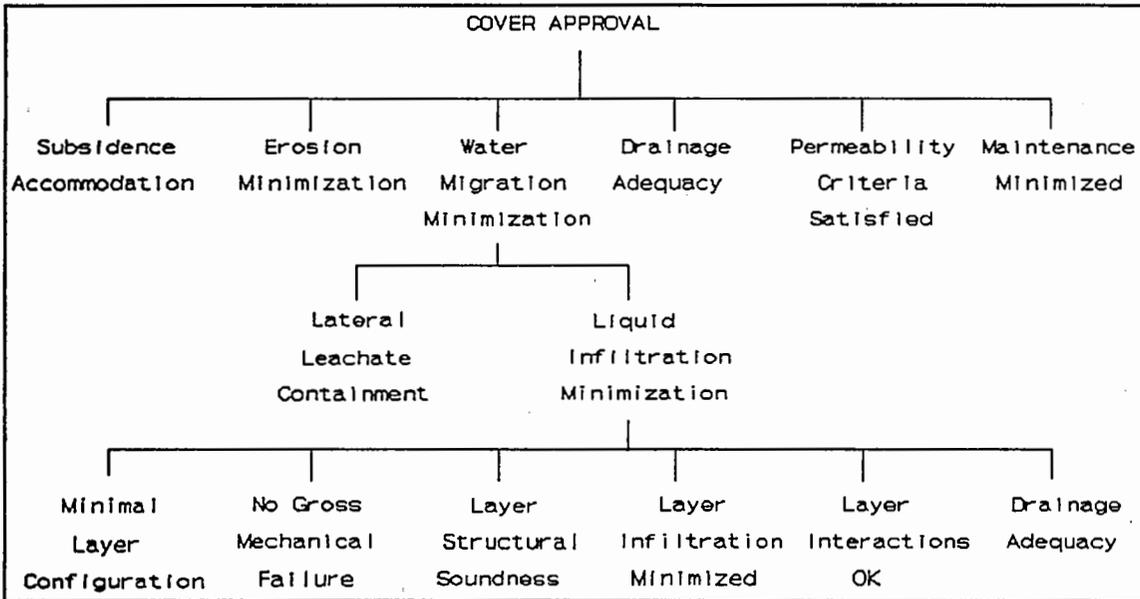


Figure 1. Goal tree for the Cover system

Lower-level system rules are usually dependent on specific inputs, and higher-level nodes or subgoals are determined by low-level conclusions. In order to fix the values of the higher-level subgoals, the logic process is switched to a "bottom-up" mode to search for specific characteristics of the design which may cause an erosion design deficiency, or otherwise determine that information is insufficient. Two examples of specific layer deficiencies for the erosion goal are that the cover has a vegetative layer thickness less than 60 cm and that calculations of soil erosion rate due to precipitation runoff result in a value greater than 2 tons/acre/year. Rule expressions for these concepts are straightforward:

**Table 1. Explanation of F-COVER's goals**

Goal	Explanation
Subsidence Accommodation	Settling of waste after closure accounted for; funds available to repair any damage to cover.
Erosion Minimization	Vegetative layer at least 60 cm deep and its rate of soil loss is under 2 tons/acre/year.
Water Migration Minimization	Release of leachate to ground and surface waters is minimized.
Lateral Leachate Containment	Leachate will not escape through sides or top of cover.
Liquid Infiltration Minimization	Amount of rainfall infiltrating the cover and causing the creation of leachate is minimized.
Minimal Layer Configuration	All recommended cover layers are present (Top, Drainage, and Low-Permeability layers)
No Gross Mechanical Failure	No gross mechanical failure of cover due to subsidence, biotic intrusions, soil creep, waste gases, leakage through penetration.
Layer Structural Soundness	No piping of soil into adjacent layers; no clogging of drainage layer; FML resistant to heat and UV attack; soil liner below frostline.
Layer Infiltration Minimization	Drainage layer of suitable thickness and permeability; FML of sufficient thickness and free of imperfections; no leakage through FML penetrations; soil liner thickness, permeability, plasticity and organic content are OK.
Layer Interactions OK	No loss of fines from vegetative to filter or drainage layer; FML chemically compatible with leachate; layer above FML doesn't creep; suitable blanket and bedding layers provided for FML; soil liner compatible with leachate.
Drainage Adequacy	Runoff capacity is adequate; no tendency for ponding of liquids.
Permeability Criteria Satisfied	Permeability of landfill's subsoil (or bottom liner) is no less than that of the cover.
Maintenance Minimization	Efforts and resources needed to maintain cover over the post-closure period are minimized.

IF top layer is a Vegetative/Soil layer  
AND layer thickness is < 60 cm  
THEN a substantive erosion deficiency exists.

IF calculations of erosion are provided  
AND calculations do not indicate an erosion rate less than 2  
tons/acre/year  
THEN a substantive erosion deficiency exists.

Figure 1 shows the high-level goal tree that was developed in this manner for COVER's rule base. It shows how the original landfill cover performance standards have been abstracted into subgoals. Each of these is briefly described in Table 1. The leaf nodes in the tree represent subgoals. These nodes are evaluated by rules looking for specific design or information deficiencies such as described above. A variety of input values and value types from specific rules are accepted at this level. These values are passed to subgoal rules for interpretation. If no deficiencies are found at a subgoal node, then a subgoal variable is assigned a value of 'YES'. Otherwise, the subgoal variable is assigned a value of either 'NO' or '??'; the last of these indicating that information is insufficient to determine a conclusion. All subgoals in the tree must be satisfied for a cover design to be approved. The control rules needed to accomplish this task are discussed next.

#### CONTROL STRUCTURE

It may appear sufficient to combine the goal-subgoal hierarchy and lower-level rules with a 'backward chaining' control strategy (see Appendix), and to thereby determine whether or not the cover should be approved. There are no problems with this strategy when the system does not detect design deficiencies, inasmuch as all performance categories are eventually searched and evaluated in order to determine a value for the top-level goal. However, if any deficiency is detected, and a subgoal node value is set as a function of this fact, then other deficiencies may not be detected because the system will not continue to search for information specifically related to the node. Such failure to detect a deficiency can occur either at a level contributing to a particular node being evaluated, or with respect to other nodes which have not yet been evaluated. Because the purpose of design review is to identify all potential cover deficiencies - not just those which are sufficient to determine a subgoal value - a simple backward-chaining evaluation strategy is inadequate.

Rather, for a complete deficiency report, the system must explicitly find values for all goals listed in Figure 1, regardless of the value determined at any particular node. Moreover, it is also necessary for potential deficiencies to be evaluated to the extent that all contributing factors for each individual subgoal node are identified.

In F-Cover, the required exhaustive evaluation control strategy is implemented through various control processes. At the top-level, a single control function is used. This control function forces evaluation of

processes to evaluate each subgoal. The subgoals evaluated are:

- Minimal layer configuration
- Subsidence accommodation
- Erosion minimization
- Lateral leachate containment
- No gross mechanical failure
- Layer structural soundness
- Layer infiltration minimization
- Layer interactions OK
- Drainage adequacy
- Infiltration minimization
- Water migration minimization
- Permeability criteria satisfied
- Maintenance minimization

The meaning of each subgoal is provided in Table 1. Because each item in the table represents both a process and a variable in the system, all corresponding processes can be executed through the control function. As a result, when the system is asked to evaluate the goal "final approval" through application of the top-level rule, values have already been determined by the control function for all categories of performance standards and their attendant design deficiency topics. The control function insures that all node evaluations are completed, regardless of the value subsequently assigned to "final approval".

The evaluation of subgoals is conducted by the application of various rules and results in the assignment of a value to each subgoal node. To indicate the result of each evaluation, subgoal node variables are set to a single value of: 'YES', 'NO', or in some cases, '??'. As previously described, the '??' value indicates that information is insufficient to determine either a YES or NO value. For some subgoals the '??' value is not allowed, and the final node value must be either 'YES' or 'NO'.

Lastly, additional control rules and procedures are used to build an internal representation of the design, generate queries in response to which the user provides design information and other data, generate the text which is output in a deficiency report, and provide context-based 'help' information for the user. Many of the procedures governing these functions are relatively complex in structure. Because these procedures mostly serve to support the evaluation logic, they are not reviewed in detail here. In particular, procedures which access help information or generate user queries are not discussed.

The backbone of the F-Cover system is captured by the three-level relationship of the high-level goal, to component subgoal rules, to sets of lower-level analytical rules which determine the values of the subgoal nodes and control output. Understanding the last part of this relationship, the connections between subgoals and lower-level rules, requires discussion of system data structures in three additional areas. These are: 1) the representation of layers and layer-specific data, 2) the

design deficiency rules, and 3) the rules which generate the deficiency report. Examples of each of these representation classes are discussed in the following three sections.

#### LAYER PARAMETER RULES

Many design deficiency rules refer to properties of a specific layer in the cover. Other deficiency analysis rules evaluate relationships between adjacent layer groups. For both kinds of rules, it is useful to have methods (data structures) which convey information about the positioning of layers with respect to adjacent layers, and which store descriptive parameter values in a concise fashion. These needs are satisfied through variables which store the layer sequence and design parameters associated with each layer of the cover as lists. List elements are ordered to correspond with cover layers and parameters, from top to bottom. For example, the type of the second cover layer (usually a biotic barrier, filter, or drainage layer) is stored in a "layer list" variable in the second position. Similarly, layer thickness is stored in a "thickness list" variable in the second position, its permeability in a "permeability list" in the second position, and so on. These lists are referenced whenever it is necessary to select information about layers as a function of position in the cover design, or to evaluate inter-layer relationships.

Some layers, such as the vegetative top layer and the low-permeability layer, may however, be composed of more than one distinct component. The vegetative layer, for example, can include both topsoil and fill soil components. Similarly the low-permeability layer usually contains both an FML and compacted soil. For these layers, distinct components are represented by sublists within the "layer list" variable. Corresponding values of thickness, permeability and other key characteristics are similarly represented in corresponding sublists. A possible layer sequence of four layers might, for example, be represented in list form as:

```
([Vegetative, top soil, fill soil], [filter],  
[drainage], [low-permeability, FML, compacted-soil])
```

There are four main list elements [in brackets] for the four layers. Each main element is itself a list; the first item of which identifies the layer and remaining elements, if any, identify components. If a layer does not have distinct components, the only sublist element is the layer name itself.

Specialized procedures are used to identify layer structure and basic design values at the start of F-COVER's consultation. First a procedure is executed to build a set of lists representing the design sequence of layers and layer components. Then list items are interpreted through rules to determine questions required to identify key layer parameters. Finally responses to these questions are used to build other lists representing the required parameter values (e.g., thickness, permeability, etc.).

## DESIGN DEFICIENCY RULES

Lower-level rules are used for identifying design deficiencies in each of the subgoal categories listed in Table 1. Compared to the straightforward way in which subgoal nodes are combined to determine the high-level goal value, deficiency analysis rules are more interdependent and less conveniently categorized. Some analytical rules provide input to a number of subgoal nodes. Others provide information to only one subgoal. Many low-level rules are analyzed only when very particular preconditions are satisfied. Also, various linkage structures exist between deficiency-analysis rules.

Some deficiency rules are 'vertically' linked so that the result of one rule serves as an input for another more general analysis rule. In this way, a set of independent rules at one level of specificity are combined in the premises of another more general deficiency. In other cases, deficiency rules at the same level of specificity are related through common antecedent conditions or conclusions.

As a result of the complexity with which lower-level rules are organized, these design deficiency rules are more difficult to classify in terms of content than the higher-level subgoals. Some deficiency rules will be applied to more than one layer in the cover. Others will apply to only one layer, but will be interpreted in terms of their effect on the cover as a whole. Still other rules are applied to cover characteristics that concern relationships between layers, as mentioned above.

Despite these complexities, deficiency rules can usually be classified into one of three groups: (1) rules applying to the cover as a whole, (2) rules referencing specific layers, and (3) rules applicable to relationships between layer characteristics. Examples of rules for each of these groups follow.

### RULES APPLYING TO THE COVER AS A WHOLE

An example of a set of rules that apply to the cover as a whole is provided by the processes which determine if lateral containment of infiltrated water is satisfactory. Abstracted from the system's code, some rules in this category are:

```
IF   there is a potential bathtub effect
OR   potentially, there are perched water pockets in the waste
AND  also, the leachate collection system has not been analyzed or
      otherwise found to be adequate
THEN Leachate Movement Containment is NO.
```

```
IF   there is a bottom composite liner below the waste
AND  there is no FML in the Low-Permeability layer
THEN there is a potential bathtub effect.
```

IF there is no bottom composite liner below the waste  
AND there is no FML in the Low-Permeability layer  
AND the natural subsoil below the waste is less permeable than the  
least permeable cover element  
THEN there is a potential bathtub effect.

IF the waste contains sheets of material that are less permeable  
than the least permeable cover element  
AND these sheets are either directly below the cover or extend  
across the entire unit  
THEN potentially, there are perched water pockets in the waste.

IF the waste contains sheets of material that are less permeable  
than the least permeable cover element  
AND clays were used for cover when the unit was operational  
OR there is an existing cover installed during a previous  
partial closure.  
THEN potentially, there are perched water pockets in the waste.

The conclusions of the last three of these four rules establish the values needed in the premises of the first rule. The first rule by itself, determines the value of the subgoal "leachate movement containment". In terms of effect, the last three rules reference the structure of the low-permeability layer. Because the conclusions of these rules are not particular to an individual layer, the rules can nevertheless be regarded as applying to the cover as a whole.

#### RULES REFERENCING SPECIFIC LAYERS

Rules applied either to the top cover layer or to another singular layer such as the drainage, low-permeability, or gas vent layer, are members of this group. Examples of layer-specific rules are provided by the rules that determine whether or not erosion of the cover has been minimized. These rules evaluate characteristics of the top layer in the design. Four of these rules are:

IF the top layer in the design is a Vegetative layer  
AND the thickness of the layer is < 60 cm  
THEN Erosion Criteria Satisfied is NO.

IF the top layer in the design is a Vegetative layer  
AND the thickness of the topsoil in this layer is < 15 cm  
THEN Erosion Criteria Satisfied is NO.

IF the top layer in the design is a Surface Armor layer  
AND the thickness of the layer is < 60 cm  
THEN Erosion Criteria Satisfied is NO.

IF the applicant has provided calculations of the rate of erosion  
from the top layer  
AND these calculations indicate that the rate of erosion is more

than 2 tons/acre/year  
THEN Erosion Criteria Satisfied is NO.

Other layer-specific rule examples are found in the group of rules used to evaluate the adequacy of the gas vent layer:

IF there is a Gas Vent layer in the cover design  
AND it is a soil type layer  
AND the USCS soil type is neither GP or SP  
THEN the soil type is inappropriate and the Gas Vent layer may not be structurally sound and the cover may not be structurally sound.

IF both a Gas Vent layer and a Drainage layer are included in the cover  
AND at least one of these layers is composed of a geosynthetic material  
AND the transmissivity of the Gas Vent layer is less than the transmissivity of the Drainage layer  
THEN the cover may not be structurally sound.

IF both a Gas Vent layer and a Drainage layer are included in the cover design  
AND both of these layers are soil-type layers  
AND the permeability of the Gas Vent layer is greater than the permeability of the Drainage layer  
THEN the cover may not be structurally sound.

Although these rules determine deficiencies particular to the gas vent layer, the conclusions are generalized to the cover as a whole because the goal "the cover may not be structurally sound" appears in each of the three rules.

The software processes that interpret overall structural soundness are, in practice, more complex than is implied by these examples. Much of the added complexity stems from techniques which are used to preserve information as conclusions are passed up the goal analysis tree. In addition to the conclusions shown in the preceding examples, many lower-level conclusions also generate a unique expression or value that becomes an element of a list variable. Lists constructed by these events are available for interpretation by subgoal nodes.

For example, each of the three rules shown for analysis of the gas-vent layer also trigger processes passing information to the "cover structural soundness" node. This subgoal node interprets the component expression values so that if any one of the contributing rules is fired, the source rule is identifiable. These unique identifiers are eventually used in the report process. Hence, even though each of these three rules can have the same higher-level result (to set the value of the subgoal node to "NO"), lower-level contributing conditions can be identified when the

report is generated. Similar processes are used in other rule groups for other subgoal nodes.

#### RULES TESTING RELATIONSHIPS BETWEEN INDIVIDUAL LAYERS

Examples of layer-relationship rules are those used to evaluate the potential for soil piping, or the gradual soil movement from one layer to another:

IF the Filter layer to be analyzed is preceded in the layer sequence (top-to-bottom) by a Vegetative/Soil top layer or a Surface Armor/Soil Top layer  
AND the Filter layer is a soil-type layer  
AND the ratio of grain size diameters (in mm) for the soil in the filter layer at the 15% sieve level, over the soil in the top layer at the 85% sieve level, ( $D_{15}[\text{filter}] / D_{85}[\text{top}]$ ), is greater than 5  
THEN the Filter layer may be subject to soil piping.

IF there is a Drainage layer in the design  
AND this Drainage layer is constructed of geosynthetic material  
AND the preceding (above) layer is not also constructed of geosynthetic material  
THEN the Drainage layer may be subject to soil piping.

IF there is a Drainage layer in the design  
AND it is immediately preceded by a Filter layer  
AND potential filter piping has been determined for the preceding layer  
THEN Drainage layer integrity is threatened by the potential for piping at the Filter layer.

In the first piping rule,  $D_{15}$  and  $D_{85}$  respectively represent the soil grain diameters for soil particle size distributions at the 15th and 85th percentiles.

Like the gas vent layer rules discussed above, the results of these piping analysis rules also may supply information to the subgoal node "layer structural soundness". Unlike the gas vent rule structure however, piping rule results are chained through other rules; and it is these intermediary rules that contribute the list elements interpreted by the higher-level subgoal.

#### CONCLUSION AND DEFICIENCY REPORTING

The conclusion of a consultation is reached when all rules required to evaluate subgoals have been tested, and all subgoals have consequently, been assigned values. Usually, there are many rules in the rule base which are neither tested or executed. In general, rules appropriate to the specified design are tested, and lower-level rules which are inappropriate

to the design are not considered. Of course, a rule only executes when premises are satisfied, and many rules which are tested will nevertheless, fail to be satisfied.

When all appropriate rules have been tested, the system writes a text report of results and recommendations. The report is stored in a file which is available for viewing, printing, or editing. The structure of F-COVER's deficiency report follows, for the most part, the goal tree of Figure 1 in a top-down rather than a bottom-up fashion. First the result of the major performance goal is reported; and if the goal has 'failed' (i.e., one or more deficiencies were detected), then subgoal deficiencies are listed. Under each subgoal heading, all specific deficiency findings are presented. If there are no subgoal deficiencies (i.e., all subgoal tests were satisfied), then only heading information and a statement that the main goal was satisfied are included in the report.

Text for the output report is generated in various ways. Some text is recovered from an external file, and other text is generated directly by the program. List variable inputs to the subgoals are decoded to determine report content and order. Report writing rules are also explicitly triggered by the operations of deficiency analysis rules or subgoal rules.

Although text is output only after completion of a consultation, some text is retrieved or generated during analysis, and other text is retrieved afterwards. In either case, report text pieces are stored in a set of program variables. These variables are combined and ordered as a function of both logical content and the sequence of tested subgoal nodes. Finally, all stored text is written to a designated file.

These functions are illustrated by the following report rule which generates text, reads additional text from an external file, and stores the combination of this information in a program variable:

```
IF    the topsoil-type of the top layer is not one of the USCS class
      values: MH ML CL OH OL SM or SC
THEN  the goal-list gets 'soil class unacceptable'
AND   the report gets 'The soil class specified',[topsoil-type], 'is
      unacceptable.'
AND   the report gets READ(report text file,'soil class text').
```

The premise checks the Unified Soil Classification System (USCS) topsoil class provided by the user [topsoil-type] against a list of acceptable values. If the topsoil-type is not in the list (MH, ML, CL, OH, OL, SM, or SC), a phrase representing this result ('soil class unacceptable') is stored in a report variable (goal-list) which is available to the subgoal node, and appropriate report text is created. The report text is a combination of a sentence ('The soil class specified,' [topsoil-type], 'is unacceptable.'), and text which is retrieved from an external file via the READ function. READ obtains text labeled 'soil class text' from a report text file. The first sentence of the report text specifies the USCS classification of the topsoil entered by the user

(topsoil-type). Combined text is stored in the variable named 'report' in this example.

Although the processes that create, generate, and arrange text are sometimes complicated, the procedure which writes the output file is straightforward. This process, in pseudo-code, is as follows:

```
WRITE (<filename variable>,<report heading variable>)
WRITE (<filename variable>,<main conclusion variable>)
WRITE (<filename variable>,<final report text variable 1>)
WRITE (<filename variable>,<final report text variable 2>)
.
.
.
WRITE (<filename variable>,<final report text variable n>)
CLOSE (<filename variable>).
```

The WRITE operation is the converse of the READ function. It writes the value of the second parameter to the file identified by the first parameter. The first WRITE statement outputs heading information. The second WRITE issues a statement corresponding to the state of the top goal node (i.e., were any deficiencies detected?). All remaining WRITE functions output text for various subgoals and accompanying deficiency analysis text. If a particular subgoal node state is YES (meaning no deficiencies were found), then the value of a particular report text variable may be null or empty. If a final report variable is empty, the corresponding WRITE function does nothing.

#### FINAL COMMENTS

Although F-COVER was created with a development tool which is primarily a backward chaining system, the directions of rule linkage processes in F-COVER are mixed. Both backward and forward rule linking processes are used. The relationship between subgoals and deficiency analysis rules is mostly driven through backward chaining. In order to determine a subgoal value, some subset of deficiency rules must be tested. A type of forward chaining is used however, for parts of the deficiency analysis where it is necessary to ensure execution of some subset of analysis rules regardless of the values of corresponding subgoal variables. Also, forward chaining techniques are used to ensure that all subgoals are evaluated during parts of the report writing process.

As well as forward and backward chaining structures, other methods are used to control rule processing. Repetitive loop-like processing is used at various stages of the analysis to ensure that rule tests are efficiently applied to a sub-sequence of layers or layer parameters. Given the list structures that store key values, loop processes control 'traversal' evaluation of selected lists or list subsets. In other words, a rule process is conditionally applied to individual list elements through a control operation. As a result, the number of explicit rules needed is reduced, and the system's organizational coherence is increased.

Lastly, other techniques are used as parts of the user interface and to tie the report generation rule base to analytic and goal level rules. For the report process, such methods are used to arrange findings in terms of increasing levels of specificity. This ordering is more natural than what is obtained when findings are displayed or written in the order determined by discovery.

Rules for deficiency analysis, rules to determine subgoal and goal values, and rules for controlling report generation, are the essential elements of the F-COVER system. Rule-based structures were found to provide a relatively flexible means for representing declarative knowledge within the domain and for controlling communications with the system user. These rules were combined with other procedures to enhance the user interface and increase the efficiency of rule application and report generation processes.

#### APPENDIX - RULE SYNTAX

Rules are expressions relating how variables, also called goals, can be given particular values depending on the values of other variables. Initially, all variables are assigned values of UNKNOWN, indicating that no evaluation has occurred. Variables normally accept any number of values in the form of a list. But a variable's definition can be narrowed, so that it will accept only a single value or, perhaps, only a single numeric value or character value. Rules are expressed in a format such as:

```
IF          <clause>
AND/OR     <clause>
.
.
THEN       <action>
AND        <action>
.
.
ELSE       <action>
```

Clause in the rule's premise usually have the form:

```
<variable> <relation> <value(s)>
```

where relations are either common logical comparison operators (e.g., AND, OR), or comparison operators which operate on lists instead of single values. Common numeric operators are: equals (=), not equal (<>), less than (<), and greater than (>). Other list-type relations, such as "is a member of" or "is the first element of", also may appear in premise clauses. If the clauses in the IF-portion of the rule are satisfied, then the actions in the THEN-portion occur. Otherwise, the ELSE-actions occur. Some common actions are:

```
Assign a variable a value or set of values,
Reset a variable value to UNKNOWN,
```

Find the value of some variable,  
Display text elements on the screen,  
Display text and request a value for a variable,  
Write text to a file,  
Read text from a file, and  
Execute a procedure.

System rules are linked together through either backward or forward chaining mechanisms. The difference between these two methods refers to the ordering by which rule evaluations occur.

Backward chaining in F-Cover occurs as function of the rule structure. If a rule references a variable in its premise for which a value has not been determined, then a process is initiated to identify the unknown value. Other rules which can conclude the needed value are also tested. Satisfied rules are fired or executed. This process can be continued so that additional rules are tested to establish the premises of the rule or rules preceding in the chain. In short, backward chaining is the process of 'reasoning' from conclusions to premises, or from goals to the conditions which determine goal values.

Forward chaining is the process of reasoning from premises to conclusions. In the F-Cover system forward chaining is accomplished by explicitly forcing a rule evaluation process to occur and thereby establishing a rule's consequent or action component.

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EVALUATION OF ASBESTOS RELEASE FROM BUILDING DEMOLITION

FOLLOWING THE OCTOBER 1989 CALIFORNIA EARTHQUAKE

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ABSTRACT

Following the severe earthquake along the San Andreas fault on October 17, 1989, the EPA Risk Reduction Engineering Laboratory was requested to assist EPA Region IX and the Monterey Bay Unified Air Pollution Control District in evaluation of fugitive emissions from building demolition and subsequent disposal of the demolition waste. Buildings damaged during the earthquake were considered to be structurally unsafe, preventing any access to ascertain asbestos content. The presumption was made that the buildings contained asbestos because similar undamaged adjacent buildings were surveyed and asbestos was found.

Demolition of damaged buildings was monitored at the Santa Cruz Pacific Garden Mall and Downtown Watsonville. Disposal operations for demolition wastes were also monitored at the Santa Cruz Municipal Landfill.

Visible emissions were observed during the demolition process. These were most apparent during structural destruction of the buildings and were generally absent during handling of the debris. Because of copious wetting during the process, no visible emissions were observed. There were measured asbestos levels above background without visible emissions during the handling of debris.

Operators of bulldozers involved in landfilling of the asbestos-containing debris were exposed to personal breathing zone concentrations above background level.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

The October 17, 1989 San Andreas fault earthquake epicenter was only about 10 miles from Watsonville, CA, 20 miles from Santa Cruz and 80 miles from San Francisco (Figure 1). Numerous buildings were structurally damaged and were scheduled for emergency demolition. Severely damaged buildings were unsafe for re-entry particularly when aftershocks could be expected; therefore, it was not possible to inspect these structures for asbestos. Because inspection of similar undamaged adjacent buildings revealed that they did contain asbestos, the presumption was made that the buildings being demolished also contained asbestos. Since the buildings were condemned and no access was permitted, asbestos removal prior to demolition could not be accomplished. There was, therefore, a concern about emissions from the demolition sites and the landfill where the debris was deposited.

The EPA Risk Reduction Engineering Laboratory (RREL) provided requested assistance to the EPA Region IX office and the Monterey Bay Unified Air Pollution Control District in monitoring these activities. RREL conducted air monitoring for asbestos during demolition of one building in downtown Watsonville, three buildings at the Santa Cruz Pacific Garden Mall, and at the Santa Cruz Municipal landfill.

## STUDY DESIGN AND METHODS

These observational studies were made as demolition work progressed. Typically, there were multiple activities ongoing including demolition, debris loading, and debris transportation. A few bulk samples were taken from debris to determine the presence of asbestos. Air sampling locations were selected to provide upwind (background ambient conditions), downwind (migration of emissions), and near activity (source emission) observations. Portable power generators were used and sampling locations were selected to be accessible to generator power and out of harm's way to the extent possible.

### SAMPLING STRATEGY

#### Watsonville

The upwind samples were taken from a parking lot 300 meters from the Canada Shoe Building demolition site. The downwind samples were taken from a parking lot adjacent to the building at a distance of 70 meters. The

nearby samples were taken across the street from the building and adjacent to a debris removal activity from a previously demolished building (see Figure 2).

### Pacific Garden Mall

The upwind samples were taken on the roof of a parking garage on the perimeter of the Pacific Garden Mall. The downwind samples were taken on the roof of a building directly across the street from the three buildings being demolished. The nearby samples were taken out a second story window of a building adjacent to the three buildings being demolished. Another nearby sample site was at ground level behind this building and adjacent to the street access of the debris transport truck route (see Figure 3, Sampling Locations in Santa Cruz).

### Municipal Landfill

The upwind samples were collected at the landfill office. The downwind samples were taken at the top of the hill where dumping occurred. Nearby samples were taken at the bottom of the debris hill. Samples were also collected with pumps mounted on corner posts inside the cab of the bulldozer which compacted the debris (Figure 4). In addition, the bulldozer operator wore a personal breathing zone (PBZ) sampler.

### SAMPLE METHODOLOGY

Area air samples were collected in a open-faced, three-piece cassette on 25 mm diameter, 0.45  $\mu\text{m}$  pore-size, mixed cellulose ester membrane (MCE) filter with a 5  $\mu\text{m}$  pore-size MCE backup diffusing filter and cellulose support pad. Electric sample pumps were operated at about 10 liters per minute (lpm) from portable gasoline powered generators. Filters were hung about 5 feet above the ground and facing downward at a 45° angle. The PBZ sampler and bulldozer cab samples were collected with a battery powered, flow controlled, personal sampling pump at 1.7 lpm. A precision rotameter was used to check pump calibration before and after sampling.

### ANALYTICAL METHOD

Samples were analyzed by the RREL Transmission Electron Microscope (TEM) laboratory. The filters were analyzed in accordance with the non-mandatory TEM method in the Asbestos Hazards Emergency Response Act (AHERA). The EPA provisional method counting rules were used.

### STATISTICAL ANALYSIS METHOD

Airborne asbestos concentrations were compared using a one-way analysis of variance (ANOVA) along with the Tukey mean comparison procedure. A constant of 0.002 equal to counting one fiber was added to all counts to analyze zero values by the ANOVA, i.e.,  $\ln x + 0.002$ .

## QUALITY ASSURANCE

Blanks were analyzed to assure quality of sampling media, field handling procedures, and laboratory handling procedures.

One hundred blanks (5% from the 2000 lot purchase) were analyzed and no structures were detected. Eight closed and fifteen open field blanks were collected at the three sites and no asbestos structures were detected. Laboratory blanks were processed with each preparation of samples and no structures were detected.

## RESULTS AND DISCUSSION

As a general observation, there were visible emissions during the demolition of buildings even though water was applied by fire hoses for dust suppression. The primary emission occurred when masonry walls were demolished. A cloud of visible particulate drifted downwind from the demolition sites during this phase of demolition. Once the walls of the structures were collapsed, the fire hoses were much more effective in controlling visible emissions. In general, the TEM analysis showed a statistically significant increase in asbestos levels downwind of the demolition activities.

### WATSONVILLE

Figure 5 presents the arithmetic mean airborne asbestos concentrations at the three sampling locations during the demolition of the building in Watsonville.

The differences in mean airborne asbestos concentrations between the samples taken at Main Street during bulldozing and at the parking lot during demolition as compared to the background site are statistically significant ( $p = 0.002$ ).

### PACIFIC GARDEN MALL

Figure 6 illustrates the arithmetic mean airborne asbestos concentrations at the four sampling locations at the Pacific Garden Mall on the three days of sampling.

On two of the three days, there was no statistically significant difference in the downwind concentrations as compared to the background asbestos levels.

There were significant differences in the mean concentrations measured on November 4th ( $p = 0.0386$ ). Specifically, the mean airborne asbestos concentration on the second floor of the Rittenhouse Building ( $0.022 \text{ s/cm}^3$ ), adjacent to the demolition site, was significantly higher than the mean concentration in the Rittenhouse parking lot ( $0.005 \text{ s/cm}^3$ ) and significantly greater than background ( $0.0006 \text{ s/cm}^3$ ).

## SANTA CRUZ MUNICIPAL LANDFILL

Figure 7 illustrates the arithmetic mean airborne asbestos concentrations measured at the Santa Cruz Municipal Landfill during bulldozing operations. There were no statistically significant differences between upwind and downwind asbestos concentrations observed; however, the samples collected in the personal breathing zone of the bulldozer operator showed a mean concentration ( $0.06 \text{ s/cm}^3$ ) that was significantly greater than the mean background concentration ( $p = 0.03$ ). Periodically, the operator walked through and handled the debris. Hence, this activity may have contributed to the elevated personal breathing zone concentrations.

### CONCLUSIONS

Visible emissions were observed during the structural collapse of buildings and were generally not apparent when firehoses were used to wet the debris during loading operations; however, asbestos levels during the debris handling were elevated above background (i.e., statistically significant) even though there were no visible emissions.

These limited data support the premise in NESHAPS (Proposed Rules, January 10, 1989; 40CFR Part 61, page 925) that the absence of visible emission is not sufficient evidence to assume no fugitive particulate emission.

Operators of bulldozers involved in landfilling of asbestos-containing debris can be exposed to personal breathing zone concentrations above asbestos fiber background level.

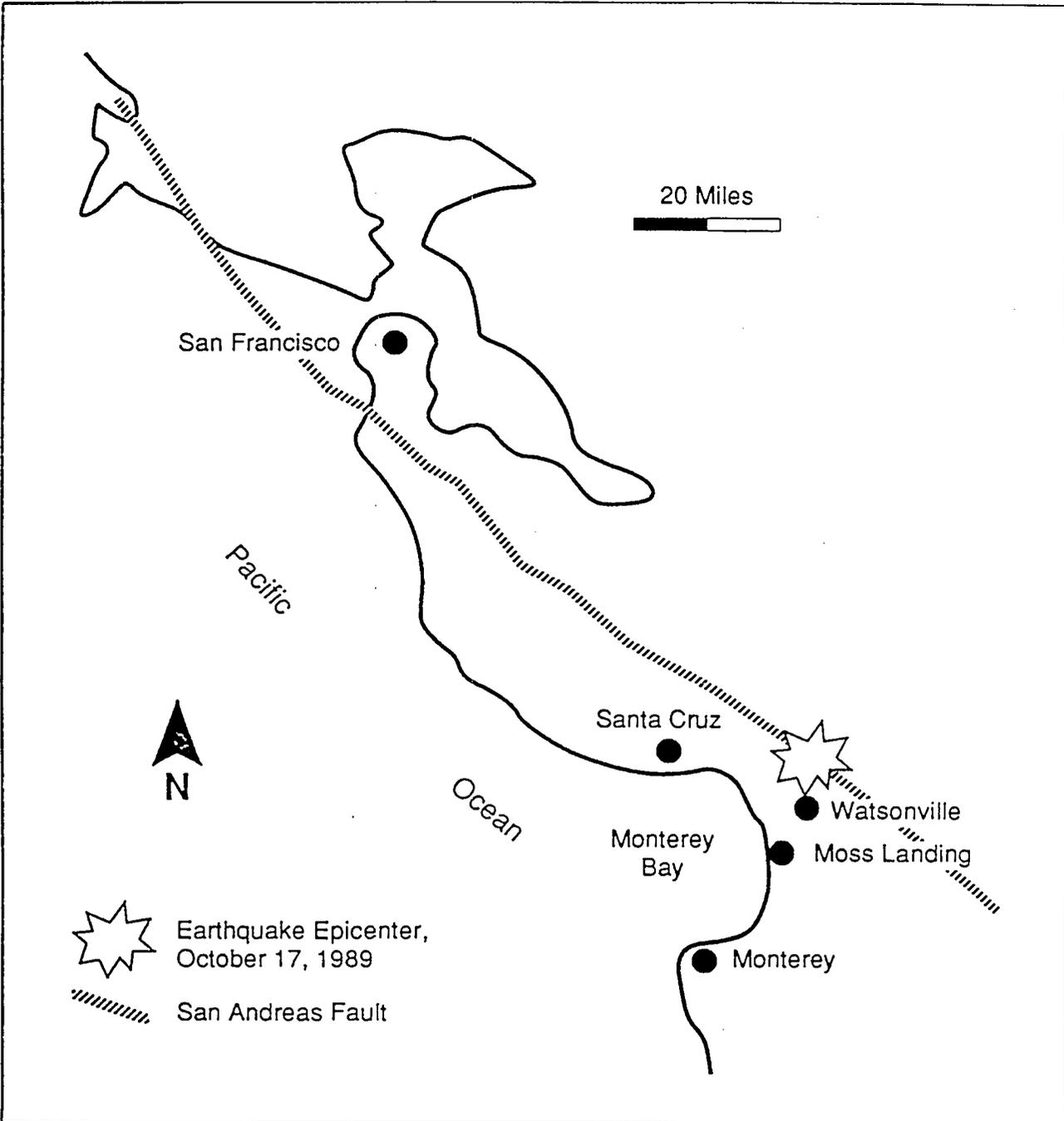


Figure 1. Geographical location of Earthquake.

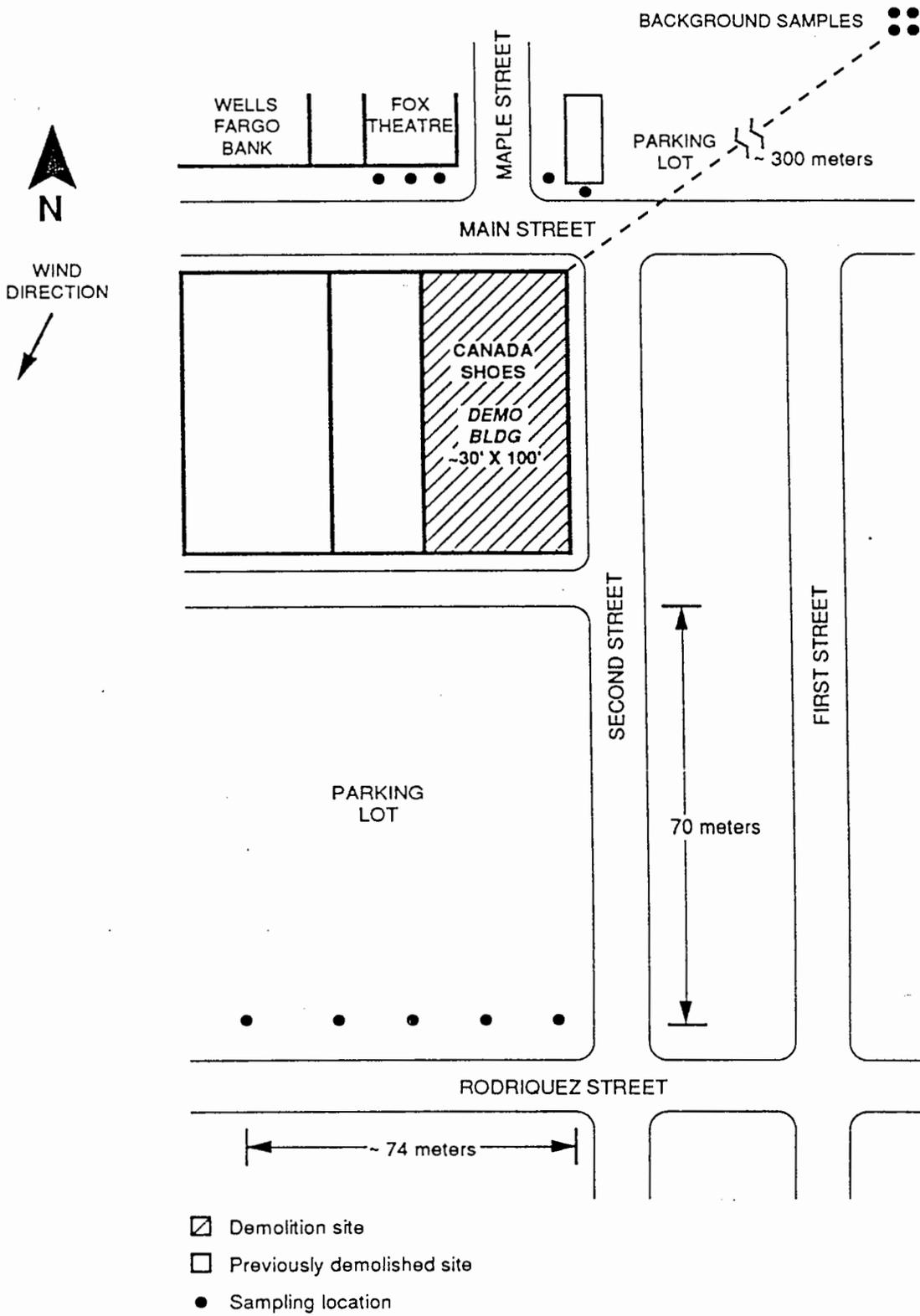
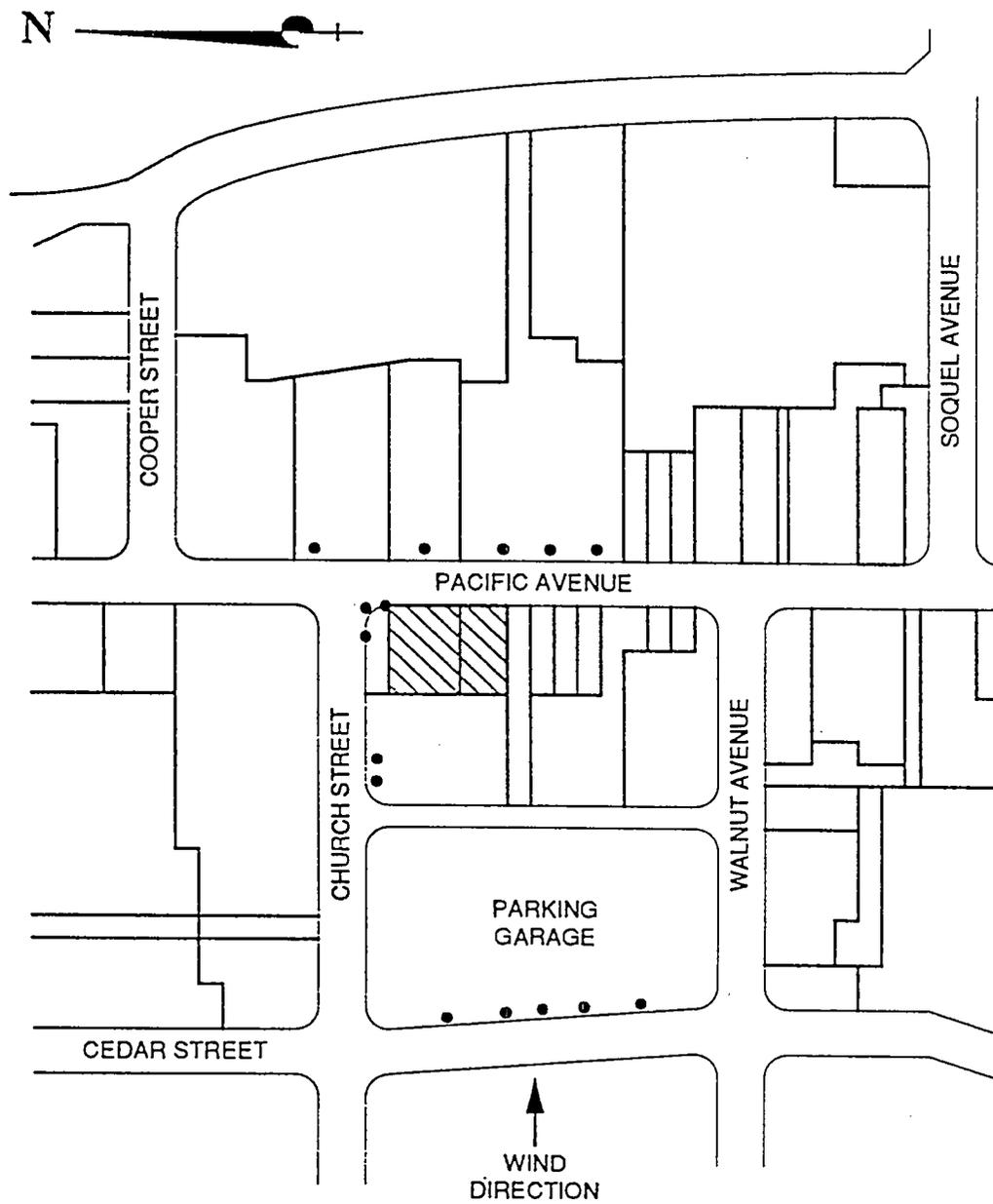


Figure 2. Location of sampling sites during the demolition of a building in Watsonville, California.



 Demolition sites.

• Denotes sampling locations.

Figure 3. Location of sampling sites at the Pacific Garden Mall in Santa Cruz, California.

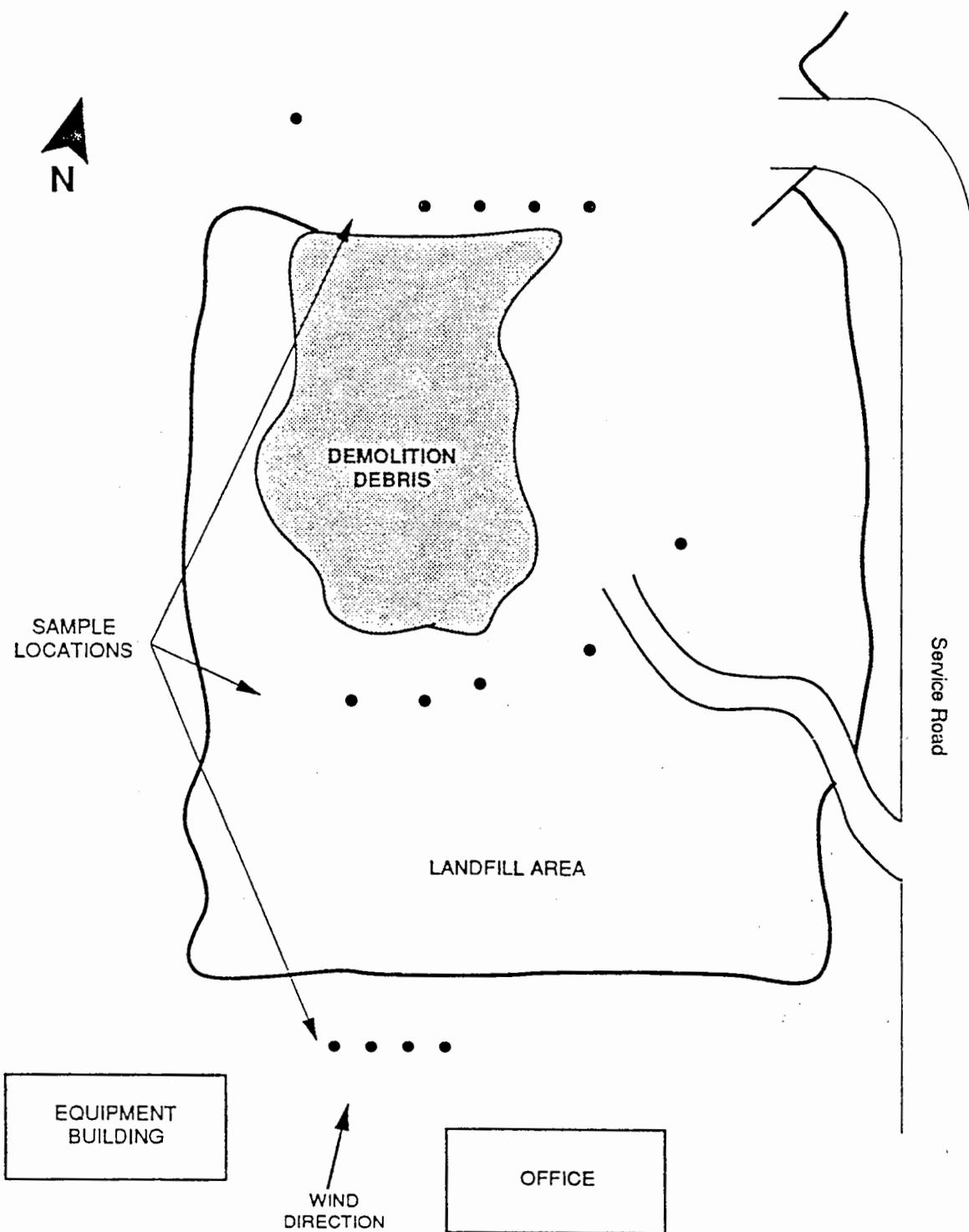


Figure 4. Location of sampling sites during the landfilling of demolition debris at the Santa Cruz Municipal Landfill.

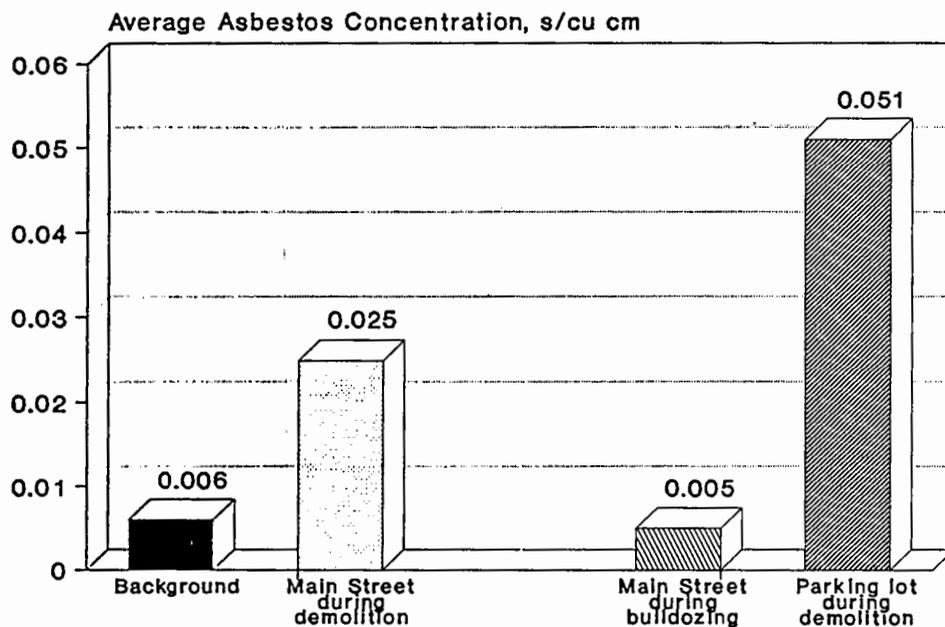


Figure 5. Average asbestos concentrations at Watsonville.

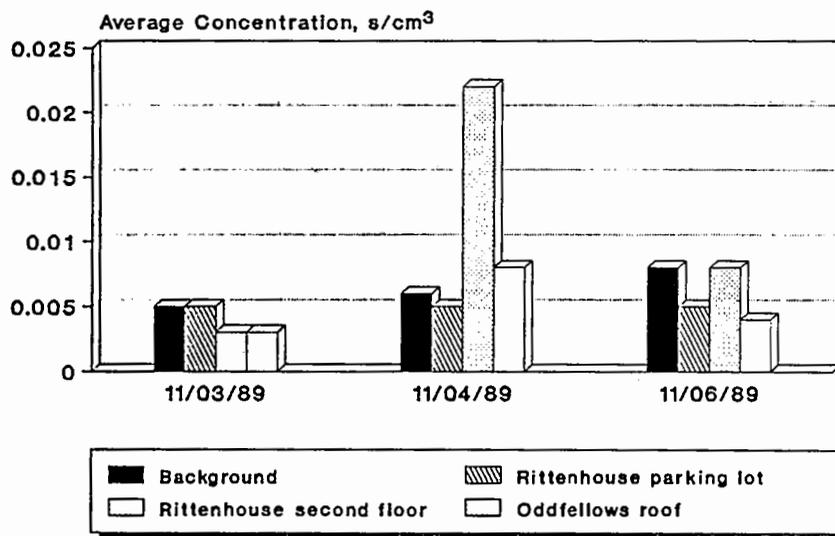


Figure 6. Average airborne asbestos concentrations during building demolition at the Pacific Garden Mall in Santa Cruz, California.

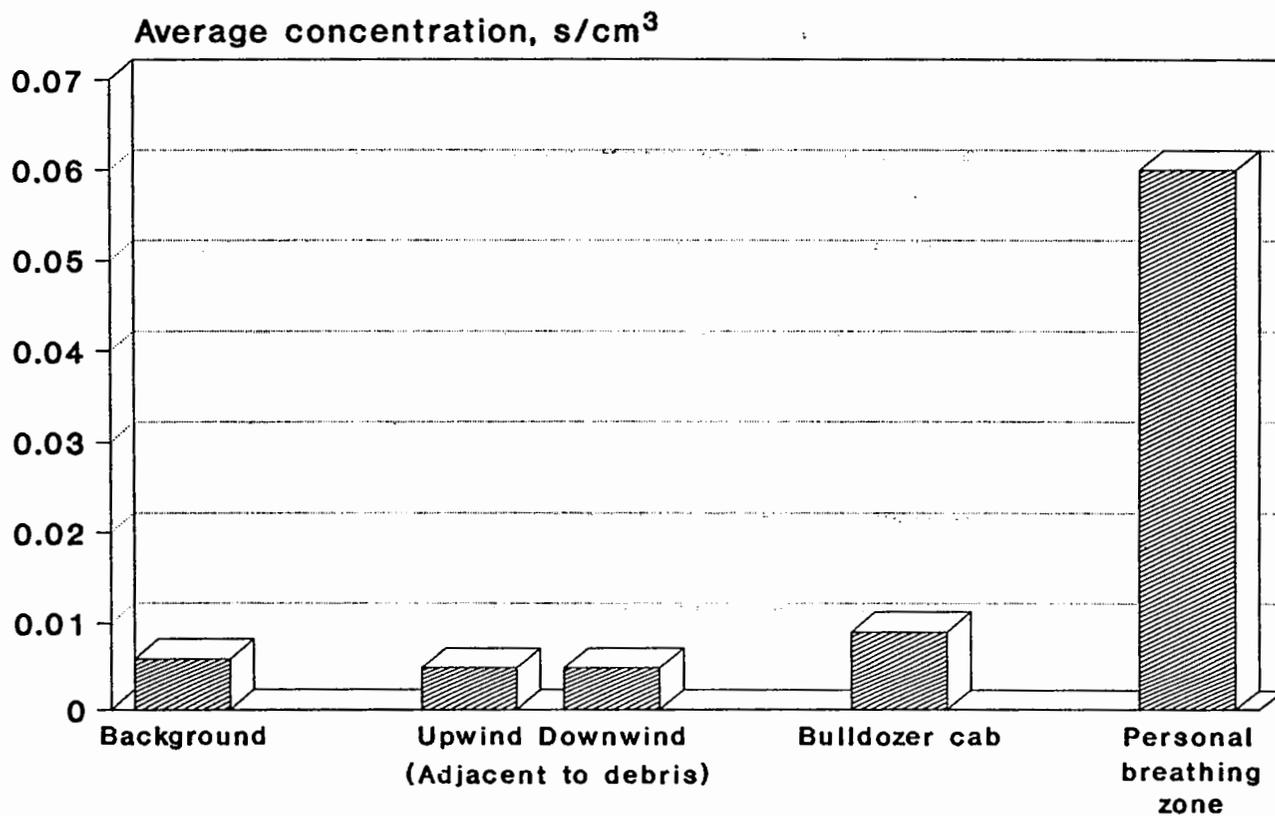


Figure 7. Average airborne asbestos concentrations during the landfilling of demolition debris at the Santa Cruz municipal landfill.

ASSESSING THE RISK OF REMEDIAL ALTERNATIVES AT SUPERFUND SITES --  
IMPLICATIONS FOR TECHNOLOGY DEMONSTRATORS

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ABSTRACT

Although the basics of risk assessment are familiar to those who must administer the cleanup of Superfund sites, frequently technology developers have little knowledge of information needs in this area. This paper describes the users and use of risk assessment at sites in order to improve technology demonstrators' understanding of these needs and make them aware of potential data requests.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

The importance of risk assessment in the selection of remedy process at Superfund sites has many implications for technology demonstrators. These implications will be related through a description of the use of risk assessment in the process, a discussion of the users of the risk information, and the information that technology developers can provide.

RISK ASSESSMENT IN THE SUPERFUND PROCESS

The introduction of a remedial technology to a Superfund site follows the formal selection of remedy process. Information is gathered during the site Remedial Investigation and Feasibility Study (RI/FS). Based on information from the RI/FS process, the remedial project manager (RPM) makes a selection of a remedy that is ultimately documented in the Record of Decision (ROD).

It should be pointed out that the formal process of remedy selection leading to a ROD is not the only way remedial actions are employed in Superfund. "Interim actions" are taken at remedial sites when such an

action is helpful in controlling contamination. These actions are taken when time is critical, and may occur before the RI/FS process can be completed. An example is the pumping of ground water to contain contaminant plume migration.

For a ROD, the remedy is selected using nine criteria established in the National Oil Spill and Hazardous Waste Contingency Plan (NCP). These are: the threshold criteria -- (1) overall protection of human health and the environment, (2) compliance with applicable or relevant and appropriate requirements (ARARs); the balancing criteria -- (3) long-term effectiveness and permanence, (4) reduction of toxicity, mobility, and volume through treatment, (5) short-term effectiveness, (6) implementability, (7) cost; and, the modifying criteria -- (8) state acceptance, and (9) community acceptance. Except for the cost criterion, these criteria can involve information from the risk assessment process.

A baseline risk assessment is part of the RI/FS process to determine the risk if no action were taken. This assessment calculates risk to human health and the environment through the assessments of hazard and exposure. For human health, calculations are made for cancer and noncancer endpoints. For environmental effects, other endpoints may be used. These methods are detailed in the Risk Assessment Guidance for Superfund, Volume I -- Human Health Evaluation Manual, Part A (1), and Volume II -- Environmental Evaluation Manual (2). These documents discuss the current site risks, but not the development of remediation goals or assessment of risks associated with remedial actions. These topics are being addressed in guidance now under development as Parts B and C, respectively. Some of the topics to be included in Part C will be discussed here.

For emergency responses, especially in light of new land disposal restrictions, various remedial technologies are now receiving more consideration for controlling pollution at sites along with the traditional removals. Risk assessment can assist in evaluating remedial alternatives.

Risk assessment may have another role in the five-year review. These reviews are required where hazardous materials have been left on site as part of the remedy. How these reviews will be carried out is under development at this time.

## THE USERS OF RISK INFORMATION

Before discussing the content of the risk information that technology developers could provide, it is helpful to know who the audience is for this information. The RPM has been mentioned. However, as the remedy is selected, it has to be approved by both the regional management up to Administrator and accepted by the public. The importance of community acceptance is not to be underestimated. In most cases, the community's list of concerns is topped by health effects.

For the RPM, the regional risk assessor or toxicologist is a resource person who evaluates and interprets site risk information. They may be called upon as expert witnesses to defend EPA actions in cases involving

potentially responsible parties (PRPs). (Recently, a decision was made that EPA would take over the assessment of risk at PRP sites.) The risk assessors are committed to ensuring that the NCP-specified risk levels are met at sites. The risk assessor may have a major role in assessing the attainment of cleanup goals at remediated sites at delisting or five-year review. In addition, risk assessors help the RPM find ways to offer the community maximum protection during remedy implementation. Risk assessors can help the community understand the balance between a choice of remedies that have some probability of failure weighed against those with long-term risk.

Besides risk assessors in regional offices, there are technical experts in the specialized areas of ecological effects and air pathways. These specialists help the RPM to interpret site information, or help to advise what data are needed to assess impacts. There are ecological or biological technical assistance groups (known as BTAGs) set up in most regions. These groups have members with field experience from agencies like the National Oceanic and Atmospheric Administration, U.S. Fish and Wildlife Service, and state departments of the environment or natural resources. They review site documents and provide advice on current and predicted ecological effects at sites. Air/Superfund coordinators assist with issues relating to air emissions from sites before and during remedy implementation.

An additional, expanding audience for risk assessment information on technologies is the technology transfer community. In order to facilitate acceptance of new technologies, information on the associated risks is becoming increasingly important.

#### TYPES OF AND RATIONALE FOR RISK INFORMATION

##### The Criterion of Long-Term Effectiveness and Permanence

The type of information needed to assess this criterion is either extremely easy or extremely difficult to ascertain. There are two components, both reduction of risk and probability of remedy failure. Remedial technologies that result in complete destruction or separation of contaminants from site media are effective and permanent, and result in complete reduction of risk. These technologies incorporate chemical processes, extraction, separation, bioremediation, etc. Their effectiveness is contingent upon the extent to which the contaminant is removed, provided that no new contaminants are added or created in the process.

The health-based target concentration for remediation is based upon the results of a risk assessment, or actually running the risk assessment "backwards". The remediation goal is calculated based on a site-specific cancer incidence risk of one-in-a-million to one-in-ten thousand or a non-cancer hazard index of one. The individual contaminants are considered in these calculations and the risk from several contaminants or pathways may be summed. Reasonable maximum exposure is typically figured for an individual as if the site were to be residential. The exposure point

concentration is then derived from exposure pathways and toxicity data to achieve a protective level. The Superfund program use EPA's IRIS data base and also publishes toxicity data quarterly in the Health Effects Assessment Summary Tables (HEAST) (3), available from the Environmental Criteria and Assessment Office (ECAO) in Cincinnati. These numbers can and do change based on research results. In some cases, what was thought to be an acceptable concentration could be found to be unprotective in the future.

Some remedial technologies have a finite reliable lifetime. Not only is there the risk to consider, but also the probability that failure will occur. Capping and containment technologies are examples. Choosing between this type of remedy and one that completely removes the contaminant cannot be done through simple comparisons of calculated risk. Where available, engineering estimates of the lifetime of the remedy (including probability of failure), in addition to the expected fate of the contamination upon failure, is helpful in assessing the long-term risks involved.

This long-term effectiveness and permanence information is particularly valuable in light of the need for community acceptance. A current example is in Region 7, where a Missouri community is steadfast against the incineration of dioxin wastes, even though the Agency considers incineration to be the only acceptable treatment alternative (4). The community is apparently not accepting the Agency's assessment that permanent remedial strategies are more desirable than others with a lesser implementation risk.

Many remedies are complicated by edging the middle ground. Some technologies involve intermedia transfer of contaminants or the production of new contaminants through reaction and transformation. These types of transfers and the production of new contaminants are under new scrutiny in long-term effectiveness assessments. Usually the assessment is qualitative, based on the toxicity of the contaminants, the medium involved, and the characteristics of further treatment.

An example of contaminant transfer is in soil washing, where contamination is transferred from the feed soil to the wash water. This may result in a long-term problem depending upon the amount of residual contamination or nature of the wash water treatment. In addition, the soil fines separated from the wash water may require further treatment.

In incineration, contaminants can be transformed into other contaminants altogether during quenching of hot gases, cooling of the ash, or in the treated medium. All products and waste streams must be handled further. For example, the ash then must be treated or stored, possibly becoming a long-term problem. Also, other changes, like the lowering of soil pH and destruction of organic matter, may have occurred in the treated medium. In all technologies where contaminants are removed to other locations, there is increasing scrutiny of the risks associated with both the transport and redisposal of treated media and treatment products.

## Setting and Attainment of Remediation Goals

Data on the criterion of long-term effectiveness and permanence are gathered at a point of compliance. The measure of attainment of the remediation goal must be expressed in a sampling and analysis strategy. In all long-term effectiveness assessments, it is important that the remediation goals be worked out jointly with a risk assessor. The risk assessor provides exposure pathway analysis. For example, the RPM and risk assessor may need to establish the depth of soil treatment to protect residents from excessive exposure. Goals for transformation products or reagent residues could be set, as these would not be covered by preliminary remediation goals that only addressed site contaminants and pathways in the baseline risk assessment.

The technology demonstrator must consider how the treated medium should be sampled to assure protective levels. This would include the sampling frequency and any strategies such as compositing. Also, it may help to make an assessment of the applicability of measurements like destruction efficiency and process operating parameters in lieu of residual concentration measurements. In addition, any waste streams must be tested if they are to require storage or will need to meet standards like land disposal restrictions.

Reliable data are being required from the treatability study to full scale. Superfund has recently released a document that relates the quality of data with its potential usefulness in risk assessment applications. It is entitled Guidance for Data Useability in Risk Assessment (5), released in October 1990.

Although strategies for compliance with remediation goals are common for most RODs, the five-year review process may require more formal plans to be available at the time of remedy selection. It is possible that technologies that will necessitate the five-year review will be more eagerly received if such a strategy is already in hand.

## The Criterion of Short-Term Effectiveness

This criterion, covering what happens during remediation, is the most frequently identified risk assessment concern for remedies. The exposed receptors can be the community, site workers, or the environment. Although the most common exposure pathway is through the air, the remedy may affect multiple pathways. Partial or total habitat destruction during implementation is a potential ecological effect.

Although remedy failure was discussed above, it is also a concern here. Remedy failure as it relates to the short-term effectiveness criterion deals with failure during implementation, which could include trucking accidents involving hazardous materials, reagent spills, or other mishaps.

Some common short-term effects are well-documented. Excavation emissions are the most studied (6). In some cases, steps can be taken to

reduce exposure that involve only minor changes in procedures. For example, to avoid contaminated dust exposure in a residential area, monitoring wind direction and spraying dry soil with water can be employed. In some cases, like the Wide Beach site in New York, other factors can be optimized. At that site, excavation began only after summer residents had left. The entire operation was winterized and lighted for 24-hour operation to permit the work to finish before the residents returned. For the protection of permanent residents, air monitors were installed at the construction fence line.

Other impacts are not as easily mitigated. In situ soil treatments, for example, can lead to migration or transfer of contaminants or treatment chemicals to uncontaminated media. This type of problem is largely regarded as an engineering concern, addressed by the criterion of implementability. However, assurances that impacts can be controlled are now required before implementation in order to adequately address the short-term effectiveness and community acceptance criteria. An exposure analysis of all new pathways with all contaminants involved is needed. On-site monitoring is required for any air releases, and may be required to check other media as well.

For ecological effects, the BTAGs can help plan ecologically sound remedy implementation. The environment of each site is unique. For example, excavation of soils and sediments, or even bringing in excavating equipment, can totally destroy habitats that are not easily replaced. Region 3's Bioassessment Group was able to suggest an alternative way of implementing a remedy to save a valuable hardwood wetland at a site. Instead of the heavy equipment planned for use on site, wheelbarrows and shovels were substituted, and the workers were shown the least disruptive route to the contamination.

#### Summary of Risk Information Needs From Technology Demonstrators

The following is presented as a quick checklist for information needs to support eventual full scale implementation at sites. It is divided into two parts to support the risk assessors concerns for both long-term (chronic, seven years to a lifetime) and short-term (subchronic, two weeks to seven years; and acute, less than two weeks) exposure. These divisions correspond, usually, to risk following implementation and during implementation, respectively.

##### Information for long-term assessments--

- 1) list of residual contaminants including transformation/reaction products in the treated medium and contaminants transferred to other media, with concentrations
- 2) long-term treatment/disposal concerns that include the probability of remedy failure at some point in the future
- 3) receptor population/exposure pathways if different from the baseline risk assessment
- 4) input on sampling and analysis plan for attainment of remediation goals and a five-year review

## Information for short-term assessments--

- 1) contaminant release points during treatment, from excavation through final disposition of residuals
- 2) estimates of duration and concentration of these releases
- 3) strategies for monitoring releases
- 4) transformation/reaction product concentrations in all streams
- 5) transportation information for equipment and hazardous materials
- 6) site preparation/restoration impacts
- 7) accident/failure probabilities and impacts

## CONCLUSIONS

The following is a "short list" of guiding principles for technology developers to promote environmentally safe and sound remediation of sites. The developer should attempt to:

- o Control contaminant fate (including the fate of introduced contaminants). It is important to know what happens within and outside of the technology black box.
- o Make the remedy low in risk and low in probability of failure.
- o Have a plan for long-term assessment of attainment of goals.
- o Consider ecological issues, not just human health impacts.
- o Seek community acceptance and address residents' concerns.

In general, the most desirable remedies are those that have little potential for releases of contaminants at any time during the remedial action. Remedies that do not disturb sensitive environments, or that either destroy contaminants completely or permanently transform them into non-toxic compounds are ideal. If the remedy does this with non-toxic reagents, so much the better.

Most remedies, of course, will not meet the desired conditions. The technology developer, however, must consider how to ameliorate the resulting impacts. If the technology is to be part of a treatment train, all of the issues must be addressed for all of the cars. Assessing the risks before and after controls may soon become the responsibility of the developer, not the user. As the public and risk assessors become aware of the risks associated with certain technologies, replacement technologies will be sought accompanied by assurances from the developer that risks are low.

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## CLOSURE OF A DIOXIN-CONTAMINATED SUPERFUND SITE

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### ABSTRACT

The report summarizes the closure portion of the field demonstration activities of the U.S. Environmental Protection Agency's (EPA) Mobile Incineration System (MIS) at the Denney Farm site in southwest Missouri. Sponsored by the EPA's Office of Research and Development, Office of Solid Waste and Emergency Response, and Region VII, the field demonstration, which began in October 1985, was completed with the certified clean closure of the site in June 1989.

Over a four-year period, the EPA Mobile Incineration System, operating at the Denney Farm site, treated more than 12.5 million pounds of dioxin-contaminated wastes from eight southwestern Missouri sites. At the conclusion of operations, the site soils, equipment, and buildings were decontaminated following approved closure plans. The closure operation and the closure certification process, detailed in this report, represent the culmination of the project.

### DISCLAIMER

The information in this document has been funded by the U.S. Environmental Protection Agency under Contract No. 68-03-3255 under the sponsorship of the Office of Research and Development. The document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

## INTRODUCTION - CLOSURE PLANS AND CLEANUP CRITERIA

Under the sponsorship of EPA's Office of Research and Development, the EPA Mobile Incineration System (MIS) was designed and constructed to demonstrate high-temperature incineration of hazardous wastes [1, 2]. Shakedown of the unit took place at the EPA Edison, New Jersey facility. After a successful demonstration of the unit's ability to incinerate PCBs and other chlorinated organic liquids, the MIS was modified to handle solids and brought to the Denney Farm site in southwest Missouri. The full-scale field demonstration of the unit was sponsored by EPA's Office of Research and Development, Office of Solid Waste and Emergency Response, and Region VII. The field demonstration began in October 1985 and culminated with the certified clean closure of the site in June 1989. This report details the closure operation and closure certification process.

After the MIS completed incineration of the dioxin-contaminated materials from eight area sites, the unit was closed by executing approved closure plans [3, 4]. Because incineration activities and site activities were conducted by different parties and were covered under two separate permits, two separate approved closure plans were required by the regulatory authorities, one for the MIS and one for the site. Closure of the MIS followed the plan presented in the 1987 final permit [3]. The procedures in this plan were updated, however, to include greater detail. These detailed procedures were included in the final closure plan for the Denney Farm site [4]. In addition to this information, the site closure plan included sampling procedures for soil, buildings and equipment, scope of the decontamination work, and action levels to trigger decontamination work.

Closure of the MIS and Denney Farm site, which took place from January 24, to June 30, 1989, involved decontamination of the MIS, Denney Farm soil, and supporting equipment and buildings. The cleanup criteria for the MIS and the site, included in the final site closure plan [4], are presented in Table 1. The Agency for Toxic Substances and Disease Registry provided health advisories used to develop these criteria, and the criteria were approved by the Missouri Department of Natural Resources.

The closure activities at the Denney Farm site provided a benchmark example for clean closure operations at other incinerator sites. The closure activities at Denney Farm were all encompassing and included decontamination of the site soil, the hot-zone buildings, equipment used at the site, and the incinerator itself with all of its ancillary systems. Following state- and federally-approved closure plans, the closure operation demonstrated that such activities could be completed successfully, and in a timely and efficient manner.

## CLOSURE OPERATION

Closure activities included excavation and incineration of dioxin-

contaminated soil, decontamination or incineration of contaminated debris, decontamination of buildings and equipment, and disassembly of buildings and the MIS. Closure activities are summarized below.

Almost 3,000,000 lb of dioxin-contaminated soil and debris were incinerated. The debris included: the loading dock, HEPA filter and associated ducting, wooden pallets, metal drums, and plastic sheeting used to protect excavated areas. The four buildings in the hot zone, which were constructed of sheet metal walls, wooden supports, and concrete foundations, were decontaminated. The following equipment was decontaminated: the four rented pieces of soil moving equipment used in the hot zone, including a backhoe, a forklift, and two small front-end loaders (Bobcats<sup>R</sup>); and the MIS feed system, consisting of three feed conveyors, the shredder, weigh chute, weigh scale, ram, ram trough, and Hapman<sup>R</sup> conveyor. The rubber conveyor belts were incinerated as part of the decontamination process.

Equipment located outside the hot zone was cleaned and wipe tested to ensure that it was not contaminated. Wipe testing of the MIS building located outside the hot zone showed that the walls were not contaminated. However, the floor beneath the feed system had to be decontaminated. The 17 pieces of rental equipment located in the safe zone, consisting of two air compressors, eight trailers serving as offices and crew quarters, four storage trailers for spare parts and other materials, and three tanks for wastewater storage, were cleaned and wipe tested. The MIS equipment was also cleaned and wipe tested. This equipment included the three trailers on which the major components of the MIS were mounted, the air pollution monitoring trailer, HEPA trailer, electric generators, Monarch<sup>R</sup> CPI separator, cyclone, WEP, air dryer, water softener, four wastewater storage tanks, process water storage tank, caustic storage tank, three discharge water holding tanks, and several pumps.

Final MIS closure activities consisted of dismantling the unit and preparing its components for shipment and storage at the EPA facility in Edison, New Jersey. Final Denney Farm closure activities included disassembly of the buildings and final grading of the site. The site was covered with a minimum of one foot of soil and seeded. Closure of the MIS and site were certified by an independent professional engineer registered in the State of Missouri.

#### SOIL, BUILDING AND EQUIPMENT DECONTAMINATION

The extent of contamination was determined through preclosure sampling and analysis conducted in November and December 1988. Soil samples, samples from various parts of the buildings, and samples from the equipment were taken and analyzed to determine the extent of contamination resulting from activities at the site. The samples were analyzed using approved test methods for solid waste (SW-846) for dioxins/furans, PCBs, organics, and metals. The results of the analyses were compared with the action levels for the site presented in Table 1.

TABLE 1. ACTION LEVELS OR CLEANUP CRITERIA  
FOR DENNEY FARM CLOSURE

Contaminant	Surface Soils (0 to 3 in. depth)	Subsurface Soils (>3 in. depth)	Buildings(a) (Wood Framework/Sheet Metal Siding/Foundations)
2,3,7,8-TCDD	<1 ppb	<10 ppb + 12-in soil cover or maximum 4-ft excavation + 4-ft soil cover	10 ng/m <sup>2</sup> (1 pg/cm <sup>2</sup> ) or >10 ng/m <sup>2</sup> + Sealant
PCBs	<2 ppm	<10 ppm + 12-in soil cover	100 ng/cm <sup>2</sup> or >1 ug/cm <sup>2</sup> + Sealant
Volatile/ Semivolatile	<50 ppm	<50 ppm	no significant contamination
Heavy Metals	non-E.P. Toxic	non-E.P. Toxic	no significant contamination

(a) Foundations had an additional criterion. Core samples were taken and the dust from the samples was analyzed and had to show concentrations of 2,3,7,8-TCDD <10 ppb.

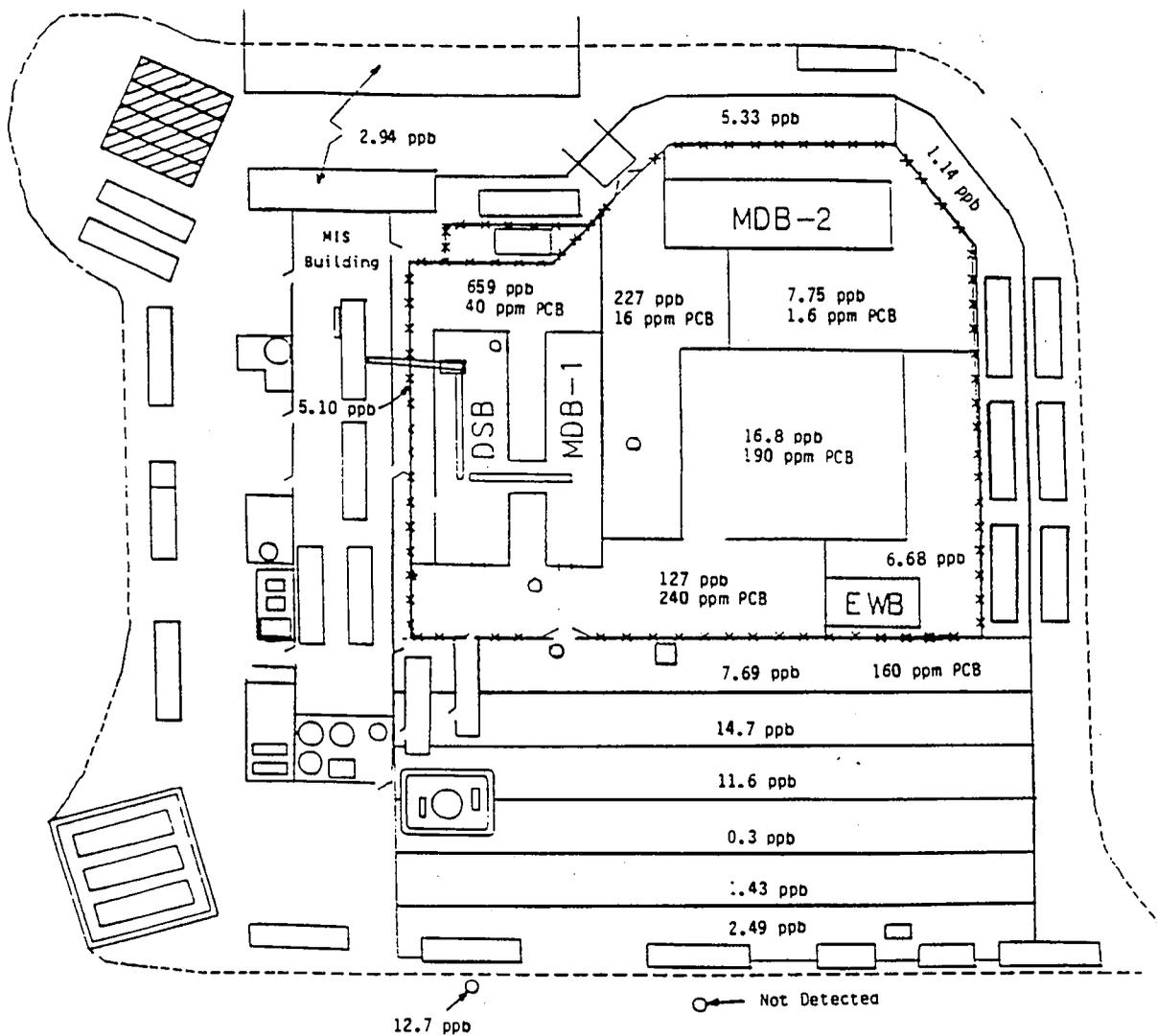
## Soil Sampling and Decontamination

Sampling was conducted prior to the start of site closure activities to determine the extent of contamination of the site soil. This sampling and analysis was primarily for dioxin using a statistical procedure to guarantee that the dioxin levels reported were within 95% confidence limits [5]. This means that there is a 5% chance that the actual concentration exceeds the maximum concentration obtained from the statistical analysis of the analytical results. In addition to employing this statistical sampling and analysis method, grab samples were taken and analyzed for dioxin and the other constituents listed in Table 1. The results of this sampling are presented in Tables 2 and 3. The sample locations are depicted on Figure 1.

The statistical dioxin sampling and analysis method is described below. A site is divided into sections. Each section is divided into 50 equal areas, and three aliquots are taken from each area. The aliquots taken correspond to locations 2, 4, and 5 as shown in Figure 2. The 50 aliquots from location 2 are composited to form one sample. The same is done for the aliquots from location 4 and location 5. Therefore, a total of three composite samples are analyzed. The results of the three composite samples are combined statistically to arrive at the 95% confidence limit for the section (see footnote a, Table 2).

The preclosure sampling at Denney Farm for dioxin was executed by dividing the site into 16 sections of approximately 5000-ft<sup>2</sup> areas consisting of 6 sections inside the hot zone and 10 sections outside the hot zone as shown in Figure 1. Dioxin contamination was found in the hot zone as expected and was also found in the 10 outside sections. At the beginning of closure activities in January 1989, the 10 outside sections were divided into 2400-ft<sup>2</sup> sections to further delineate the dioxin-contaminated area (Figure 3). In addition, another 16 sections outside the hot zone were added during the closure process to determine the extent of the contamination. The final allocation of areas with their levels of contamination is shown in Figure 3. The areas with dioxin concentrations greater than the action level were designated as contaminated areas and were targeted for remediation.

Contaminated soil was scraped in layers of at least three inches and incinerated. After each scraping, the underlying soil was sampled and analyzed for dioxin. Dioxin was selected as the indicator chemical for the soil decontamination/excavation process due to its prevalence at the site and the stringent action level for it. Scraping and incineration continued until sampling and analysis showed that the contamination of the remaining soil was below the action level for dioxin. Once an area was below the dioxin action level, it was sampled and analyzed for the other constituents listed on Table 1. Decontaminated areas were covered temporarily with plastic sheeting to prevent the spread of contamination from contaminated areas until the excavation was completed and the entire site was covered with clean soil in accordance with the cleanup criteria. The dioxin concentrations remaining after excavation are indicated in Figure 4.



-x-x-x-	Hot Zone Fence	o	Grab Sample Location (See Table 62)
DSB	Drum Storage Building	Data =	2,3,7,8-TCDD concentrations
MDB-1	Hazardous Waste Storage Building	PCB =	PCB concentrations
MDB-2	Hazardous Waste Storage Building		
EWB	Equipment Washdown Building		

Figure 1 Denney Farm Site Preclosure Sampling Results November and December 1988

TABLE 2. INITIAL PRECLOSURE SOIL SAMPLING RESULTS [November 1988]

Section No.	Sampling Date	2,3,7,8-TCDD(a) (ppb)	Chromium(b) (ppm)	PCBs(c) (ppm)
Perimeter Sections(d)				
1 SW	11-7-88	7.69	16	160
2 SE	11-7-88	1.14	11	ND
3 NE	11-7-88	5.33	19	ND
4 NW	11-7-88	5.10	13	ND
5 Ash Storage	11-7-88	2.94	200	ND
Hot Zone Sections				
6 SW	11-7-88	127.44	30	240(e)
7 NW	11-7-88	659.00	4.7	40(f)
8 SW-NE	11-7-88	227.37	8.5	16
9 Trench	11-7-88	16.77	13	190
10 NE	11-8-88	7.75	7.8	1.6
11 SE	11-8-88	6.68	15	ND

- (a) All 2,3,7,8-TCDD concentrations are at the 95% Upper Confidence Limit (UCL):  
 $C_i = \bar{X} + 2.92 S/1.731$   
 where:  
 $C_i$  = Maximum concentration of contamination at 95% UCL.  
 $\bar{X}$  = Mean concentration of three composite samples.  
 $S$  = Standard Deviation of three composite samples.
- (b) Chromium is total chromium, not EP toxicity chromium. The levels detected were considered to be safe.
- (c) PCBs expressed as Aroclor-1260.
- (d) SW=southwest, NW=northwest, SE=southeast, NE=northeast.
- (e) Also contained 200 ppm tetrachlorobenzene and 30 ppm hexachlorophene.
- (f) Aroclor-1016.

Note: Other organics were detected at low levels (<10 ppm).

Action levels: See Table 1.

TABLE 3. FOLLOW-UP PRECLOSURE SOIL SAMPLING  
RESULTS [December 1988]

<u>Sample Type</u>	<u>TCDD Concentration (ppb)</u>
I. 95% UCL Soil Samples (0 to 2 in.)	
1. Section 12	14.69
2. Section 13	11.61
3. Section 14	0.31
4. Section 15	1.43
5. Section 16	2.49
II. Depth Samples in Section 1(a)	
1. 0 to 3 in.	10.49
2. 3 to 6 in.	3.00
3. 6 to 9 in.	3.06
4. 9 to 12 in.	ND(b)
III. Depth Samples in Section 6(a)	
1. 0 to 3 in.	119.66
2. 3 to 6 in.	3.21
3. 6 to 9 in.	3.51
IV. Depth Samples in Section 8(a)	
1. 0 to 3 in.	10.13
2. 3 to 6 in.	2.01
3. 6 to 9 in.	0.67
4. 9 to 12 in.	1.25
V. Grab Samples in Section 7 (0 to 2 in.) (10 aliquots each)	
1. Around waste oil containment	11.23
2. Underneath HEPA duct	8.23
3. Between MDB-1 and DSB	3798
VI. Wooded Area South of Trailers (0 to 2 in.) (5 to 7 aliquots)	
1. Soils south of the site	ND(b)
2. Runoff behind trailer #5	12.74
(a) Grab samples	
(b) ND = not detected	

50 SOIL SAMPLES COMPOSITED  
TO FORM COMPOSITE 2

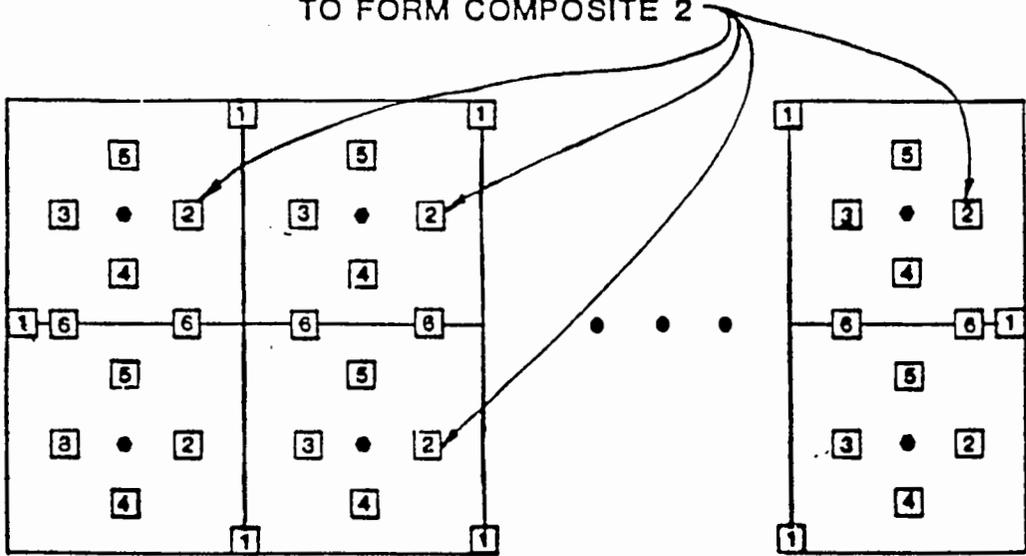
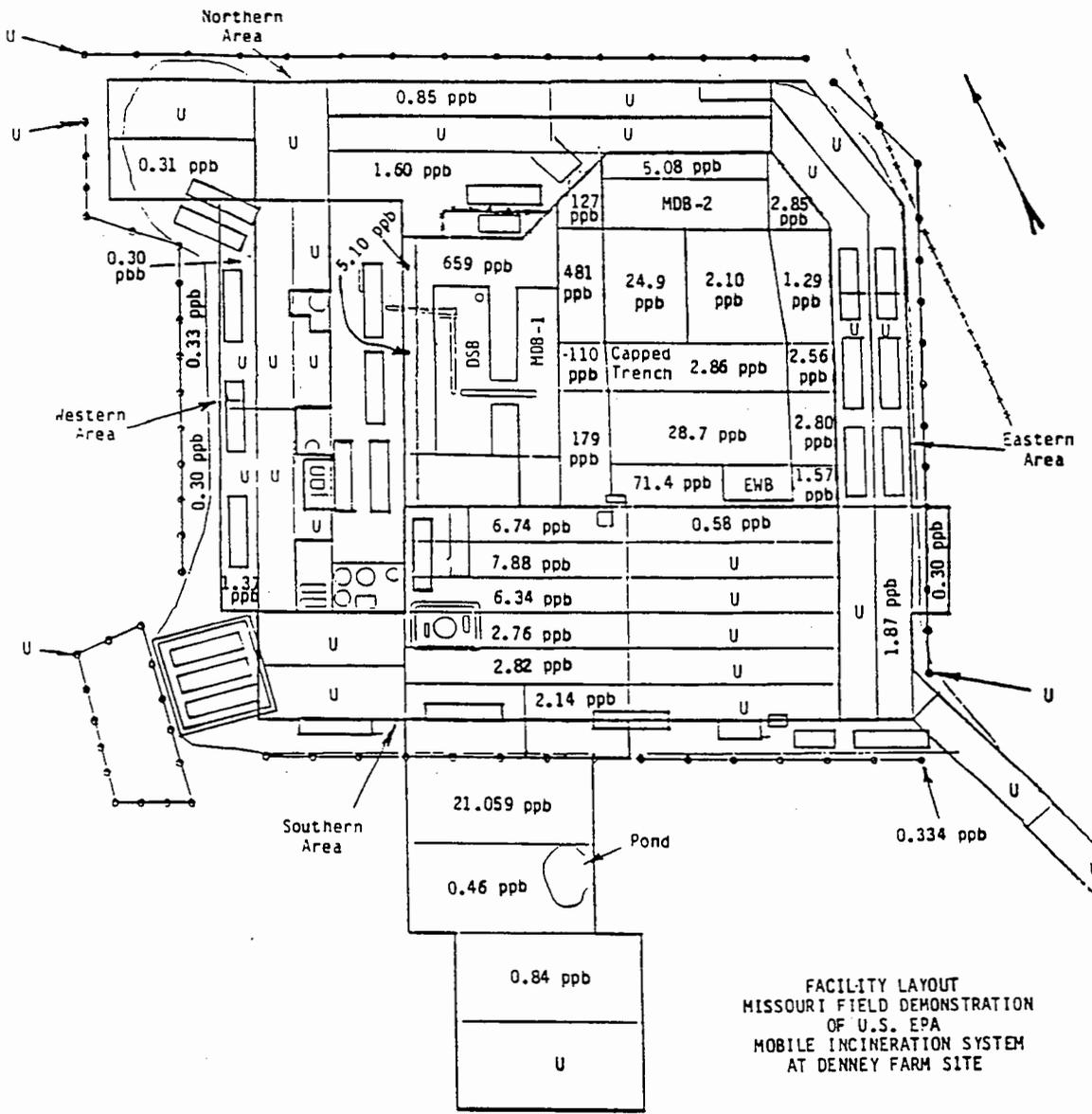


Figure 2 Systematic Sampling Design for Obtaining the 3 Composite Samples.



FACILITY LAYOUT  
 MISSOURI FIELD DEMONSTRATION  
 OF U.S. EPA  
 MOBILE INCINERATION SYSTEM  
 AT DENNEY FARM SITE

Data = 2,3,7,8-TCDD concentrations.  
 U = Not detected at 0.300 ppb detection limit.

Figure 3 Final Allocation of Areas With Their Levels of Dioxin Contamination.



## Buildings and Equipment Sampling and Decontamination

Wipe sampling of the sheet metal walls, concrete foundations, and wood framework of the buildings was conducted in order to determine the level and extent of contamination in the buildings. The metal, wood, and concrete were each wipe tested separately. Coring samples of the foundations were also taken. The methods used are described below.

Wipe samples were taken using 3-in. by 3-in. sterile gauze pads that were soaked with isooctane. The sampling procedure consisted of wiping several areas over a designated portion of the building with the gauze so that the total area wiped was 2500 cm<sup>2</sup>. The gauze was placed in an 8 oz jar. This procedure was used to collect samples for metals, organics/PCBs, and 2,3,7,8-TCDD analyses.

Concrete floor dust samples were collected from random locations throughout the buildings by using an impact drill with 1-in. carbide tipped bits to obtain dust from the entire depth of concrete. The dust was composited into three 8-oz jars for metals, organics/PCBs, and 2,3,7,8-TCDD analyses.

Buildings were decontaminated by scrubbing with brushes using a detergent solution and rinsing with high pressure water or steam cleaning. This was preceded by scraping when necessary. The decontamination process was repeated until sampling and analyses showed that residual contamination was below the action levels.

All building materials were decontaminated to the action levels indicated on Table 1 except for some of the wood. The contaminated wood was incinerated. The buildings were disassembled and removed from the site. The foundations remained and were covered with a minimum of one foot of clean soil.

All equipment was decontaminated by scrubbing with brushes using detergent solution, and rinsing with high pressure water or steam cleaning. The process was repeated until sampling and analyses showed that the residual contamination was below the action levels. It should be noted that although the MIS closure plan [3] stipulated an equipment cleanup level of 10 pg/cm<sup>2</sup> for dioxin, the equipment was cleaned to meet the more stringent cleanup level of 1 pg/cm<sup>2</sup> indicated in the site closure plan [6].

Wastewater generated during the decontamination process was passed through a filter train consisting of 50 micron and 20 micron paper filters, a sand filter, and two activated carbon filters. The filters were mounted in series. The spent filter materials were incinerated periodically. All water was discharged in accordance with the NPDES permit for the site.

Some contaminated material was generated after the incinerator was shut down for dismantling. This material included paper filters, carbon filters, sludge from wastewater tanks, and floor sweepings. This material was put into marked and sealed drums and sent to a permitted storage facility.

#### DISASSEMBLY AND TRANSPORT OF INCINERATION SYSTEM

The disassembly and transport strategy for the MIS components depended upon whether the equipment was rented, trailer-mounted or mounted in other ways. Generally, the decontaminated components of the MIS were disassembled only to the degree that all elements could be mounted on over-the-road equipment and transported back to the EPA Edison, New Jersey, facility. The non-rented equipment required 21 trailers for transport. The disassembly and transportation strategies are discussed below.

The rental equipment, listed above in the closure summary, was returned to the appropriate vendors after being restored to its "as supplied" condition.

Many of the major components consisting of the kiln, secondary combustion chamber (SCC), MX scrubber, and flue gas analyzers were mounted on seven trailers. Disassembly of the trailer-mounted units was conducted as follows: The kiln and SCC were deslagged. The equipment was cleaned and painted. The front one-third of the SCC was removed and placed on another trailer to bring the SCC trailer within highway weight restrictions. All service piping and three-phase cables were disconnected, plugged, capped, and tagged. All instrumentation was protected and sealed. The trailers were inspected, serviced, and prepared for road operation.

The remaining equipment, consisting of the wet electrostatic precipitator (WEP), cyclone, CPI separator, pumps, piping, hoses, interconnecting electrical cable, storage tanks, etc., were loaded on flat bed trailers after cleaning and disassembly.

The WEP and cyclone required special handling. The electrode assemblies were removed and packed in separate crates, and the WEP was filled with styrofoam packing. The support frame of the WEP was modified to allow shipment of the unit within its frame. Cross-beams to which the platforms were attached were replaced with shorter beams to bring the unit within the permissible shipping clearances. The WEP was loaded on a flat bed trailer and shipped in a horizontal position. The cyclone also was shipped completely within its support frame. Preparation of the cyclone for shipment consisted of removing the spring supports and replacing them with rigid links. Shims were then welded between the unit and its vertical guides.

The process water system and electrical system were disassembled and inspected. All steel and plastic piping was scrapped because of reduced

wall thickness or internal scale buildup. Only rubber hoses and trailer-mounted piping for the process water system were salvaged. All electrical cables were coiled and placed on trailers for shipping.

All remaining equipment was disassembled, placed on pallets, crated, as required, and loaded onto flat bed trailers for shipment.

## LESSONS LEARNED

Several important lessons were learned from this closure experience that could make future closure operations of this nature more efficient. These lessons are discussed below.

The hot zone at Denney Farm was separated from the surrounding area by a fence, and the buildings holding the hazardous wastes were designed for spill control. However, some materials handling occurred outside the buildings creating the potential for contamination of hot zone soils. Contamination in the hot zone, which was at a higher elevation than the rest of the site, created the potential for contamination to migrate outside the hot zone during periods of heavy rainfall. In fact, the spread of contamination outside the hot zone boundary was discovered during closure. A narrow plume of contaminants migrated out of the hot zone and was carried along by stormwater runoff into the adjacent wooded area. The discovery of this plume necessitated additional sampling and analysis work during closure to define the area of contamination, as well as additional remediation work to correct the condition.

Contamination outside of the buildings can be minimized by confining feed handling to inside the buildings. The use of conveyors to transport the contaminated soil between buildings did reduce handling outside the buildings after they were installed in March, 1988. A dike at the fence line would have been effective in minimizing the spread of contamination from the hot zone to the outside.

Conducting routine soil sampling in both the hot zone and safe zone during the operational phase of the field demonstration would have been useful to minimize contamination of the site. Having such a program in place would have allowed earlier discovery of the soil contamination. This in turn would have allowed site personnel to remediate the situation and prevent the spread of contamination beyond the hot zone, thus reducing closure costs.

It would have been useful to have had routine wipe testing of the equipment and buildings during the operational phase of the MIS program. If this had been done, potential sources of contamination around the MIS and in the personnel decontamination area could have been identified and remediated quickly, and additional contamination of these areas could have been prevented. This in turn would have helped simplify final closure operations.

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THERMAL DESORPTION ATTAINABLE  
REMEDICATION LEVELS

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ABSTRACT

Thermal desorption is a physical separation process that uses indirect heating to vaporize organic contaminants which can then be removed and recovered. Initially, low temperature was used as a descriptor for these systems to avoid being associated with combustion processes, e.g., incinerators, plasma torches, etc. This can be misleading since thermal desorbers can operate between 200° - 1000° F.

In the past few years there has been an expanded use in the application of thermal desorbers to contaminated soils and sediments. The main reason for this growth is the wide range of organics that can be effectively removed from the soils or sediments. Many Records of Decision have identified thermal desorption as the treatment of choice, and Feasibility Studies frequently include thermal desorption in the list of applicable treatment technologies.

This paper describes the thermal desorption technology (TD) and presents data on the treatment performance and effectiveness for organic compounds considered difficult to treat.

This paper has been reviewed in accordance with the US Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

Thermal desorption (TD) is being used or has been proposed as the most appropriate treatment technology for many superfund sites. TD treatment technology is recommended and used because of (1) the wide range of organic contaminants effectively treated, (2) availability and mobility of commercial systems, and (3) the public acceptance of the treatment approach. Thermal desorption is applicable to many organic wastes and generally not used for treating inorganics and metals. Commercial systems are now in operation remediating Superfund sites, and more are under construction and being designed. The public has shown a preference for this technology over incineration because as a separation process there is less likelihood of creating dioxins and other oxidation products. In response to this increased interest and use, the USEPA is now preparing an Engineering Bulletin on thermal desorption. The bulletins will provide a 5 to 10 page summary of the TD technology, the available test data, and a comprehensive reference list.

Because of the wide application of TD processes there are ongoing studies examining TD effectiveness on Superfund wastes under the SARA (Superfund Amendments and Reauthorization Act) Land Ban program. Recently available data and other treatment data make thermal desorption an excellent candidate for the Best Demonstrated Treatment Technology (BDAT) designation.

It is always a good approach to perform a treatability study to definitely determine if the selected technology can effectively remove/destroy/immobilize the hazardous constituent. The USEPA is now preparing an information bulletin on possible treatability procedures for thermal desorption processes. Bench-scale procedures would simply use a muffle furnace, exposing the sample to a set temperature for a certain period of time.

There are several Superfund Innovative Technology Evaluation (SITE) program field demonstrations scheduled for thermal desorption processes this year (1991). At the Wide Beach superfund site near Brant, New York the "Taciuk" thermal desorption process of SoilTech, Inc. (Canonie Engineers) is being used to remediate PCB contaminated soils. The USEPA proposes to perform a field evaluation on this process in March 1991. The "X\*TRAX" process of Chemical Waste Management, Inc. will be used at the Re-solve Superfund site near North Dartmouth, Massachusetts and a USEPA SITE Demonstration is tentatively scheduled for June 1991. In July a SITE demonstration of the DAVE (Desorption and Vaporization Extraction) process of Recycling Sciences, Inc. (RSI) is scheduled to take place. These SITE field demonstrations are being designed to answer some of the final, but most difficult, questions about thermal desorption; (1) are there products of incomplete combustion, e.g., dioxins, or (2) what are the impacts of high organic concentrations.

## PROCESS DESCRIPTION

Thermal desorption is any number of processes that use either indirect or direct heat exchange to vaporize organic contaminants from soil, sludge or sediments. These are physical separation processes and are not designed to provide high levels of organic destruction (e.g., 99%). Because of the high temperatures of a few systems some localized oxidation and/or pyrolysis may occur. System performance is typically measured by comparison of untreated waste contaminant levels with those of the processed waste.

Figure 1 is a general schematic of a thermal desorption process. Waste material must be excavated and screened to remove oversized objects (e.g., rocks > 1.5 inches) before being conveyed to the desorber (step 1). There are generally four designs for the desorber (step 2); an indirectly fired rotary dryer, a single (or set of) internally heated screw auger(s), a vertical mixed bed, and a series of externally heated distillation chambers. In the desorber the waste is heated (200°F to 1000°F) causing organics and water to vaporize. The gaseous organics and water are moved out of the system to the collection and control equipment (step 3), sometimes with an inert gas (e.g., nitrogen). Volatiles may then be burned in an afterburner, collected on activated carbon, or recovered in condensation equipment.

The key variable controlling the effectiveness of the thermal desorption process is the final temperature of the waste. This temperature is mainly dependent on the residence time and the heat transfer method.

Operation of a thermal desorber typically creates up to six process residual streams; treated waste, oversized media rejects, condensed contaminants and water, particulate control dust, clean offgas, and spent carbon (if used). The treated waste may be suitable for disposal on site. Water is needed to control the dusting of the treated waste and the condensed water is frequently used after treatment. The concentrated organic liquids are stored for further treatment or recovery. Collected particulate can be recycled through the desorber.

## APPLICABILITY AND LIMITATIONS

Thermal desorption has been proven effective in treating contaminated soils, sludges and filter cakes. Chemical contaminants for which bench-scale through full-scale treatment data exist include volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs), and even higher boiling point compounds such as PCBs and dioxins.

This technology is not effective in separating inorganics from contaminated media. Some metals (e.g., mercury) may be volatilized by the thermal desorption process as the contaminated media is heated. Normally the temperature of the waste achieved by the process does not oxidize the metals .

The waste must contain at least 20 percent solids, and sometimes at least 30 percent solids, to be fed into the desorber. Higher solids content is preferred because of the cost of evaporating, collecting and treating the water.

Although VOCs and SVOCs are the primary target of the thermal desorption technology, the total organic loading in the feed is limited by some systems to 10 percent or less. There is evidence that polymers (e.g., phenolic tars) may foul or plug some of the systems.

#### TREATMENT PERFORMANCE

To support some of the above claims on treatment effectiveness, data from four data sets are discussed; manufactured gas plants, two PCB contaminated soils, and dioxin contaminated soils. It is felt that these data will provide support for considering thermal desorption for future remediations (References 1,2,3 and 4).

#### HWR&IC Manufactured Gas Plants Treatment Study<sup>1</sup>

The Hazardous Waste Research & Information Center (HWR&IC) and the Gas Research Institute (GRI) performed a study of the use of thermal desorption of contamination from manufactured gas plants. Wastes at these sites were coal tar contaminated soils with between 400 and 2000 ppm total PAHs (Table 1). Eleven pilot-scale tests were performed with the IT Corporation desorber on three wastes using test conditions from 572°F to 752°F (300°C to 400°C), and 5 to 9 minutes residence times. Approximately 30 to 60 kilograms/hour of soil was used for the pilot-scale tests. Table 2 presents the pilot-scale test data with temperature and time variables. Both temperature and residence time have a major impact on the treatment results. Most commercially available treatment systems can control both parameters and thus adjust the operating conditions to meet the remediation requirements. One very important piece of information from this study was the comparability of the bench-scale and pilot-scale data. These data should support the use of an inexpensive bench-scale test to be used as an initial "proof-of-process" test.

## Chemical Waste Management X\*TRAX Treatment of PCBs<sup>2</sup>

Chemical Waste Management (CWM) evaluated the treatment effectiveness of their pilot-scale (about 5 tons/day) X\*TRAX thermal desorber. Of particular interest was the treatment effectiveness on heavy organics including PCBs. Tables 3 and 4 show PCB treatment data for the pilot-scale desorber. Good percentage removal was achieved (>99 %). While the PCB residual levels (8 to 19 ppm) shown may not be acceptable to the regulatory agencies, the residence time and temperature of the process can be increased to improve the removal efficiency. Table 5 shows some residual levels achieved for the more frequently seen contaminants.

## RSI Treatability Tests<sup>3</sup>

Between July 1984 and April 1985 the pilot-scale version (10 tons/day) of the RSI's DAVE process treated PCB contaminated sediments from Waukegan Harbor, IL and the Hudson River, NY. Table 6 presents the treatability data for these two wastes and associated process data. The PCB concentration in the clean soils averaged 1.89 ppm (1.11 ppm standard deviation), below the 2 ppm informal guideline goal. In some cases low removal efficiencies occurred, primarily because of the low starting concentrations.

## NCBC Dioxin Treatment Study<sup>4</sup>

In June 1985, Herbicide Orange contaminated soil was treated using the pilot-scale IT Corporation thermal desorber. Of specific concern was the dioxin (2,3,7,8-TCDD), and the 2,4-D and 2,4,5-T pesticides. Table 7 shows the operating conditions and treatment results for the dioxins, furans, 2,4,5-T and 2,4-D. The project goal of less than one part per billion (<1ppb) TCDD was achieved, with removal efficiencies of 99.68 to 99.97 %. Concentrations of 2,4,5-T and 2,4-D were reduced to less than 0.2 ppm, the detection limit. It should be pointed out that the operating temperature of 1040°F (560°C) is unusually high for most commercial thermal desorbers.

## SUMMARY AND CONCLUSIONS

The thermal desorption treatment technology has wide application to Superfund sites contaminated with organic compounds. While there may only be a few commercially available thermal desorption systems that can operate at 1040°F (560°C), these systems could possibly treat dioxin wastes. Far more thermal desorbers can operate in the 800°F (427°C) range for

treating PCB contaminated soils. By the end of this year there will be data from field demonstrations of PCB contaminated soils. It is projected that thermal desorption can remove VOCs, SVOCs and TPHs (total petroleum hydrocarbons) from soils, sludges and sediments to the part per billion range in most cases.

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Figure 1  
Schematic Diagram of Low Temperature Thermal Desorption

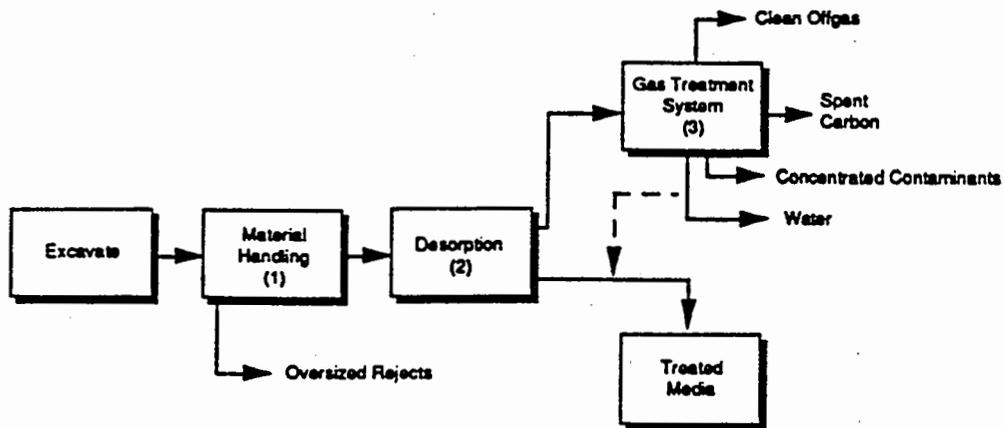


Table 1: HWR&IC Untreated Soil Concentrations

Compound	PAH Concentrations (ppm)		
	Soil A	Soil B	Soil C
Acenaphthene	210	390	ND <sup>a</sup>
Anthracene	ND	190	ND
Benzo(a)anthracene	ND	55	15
Benzo(b)fluoranthene	46	34	34
Benzo(k)fluoranthene	39	18	25
Benzo(a)pyrene	ND	40	32
Benzo(g,h,i)perylene	18	18	110
Chrysene	ND	ND	19
Dibenzo(a,h)anthracene	ND	ND	11
Fluoranthene	260	230	28
Fluorene	170	230	ND
Indeno(1,2,3-cd)pyrene	14	18	37
Naphthalene	680	66	ND
Phenanthrene	410	490	ND
Pyrene	260	220	55
<b>Total Quantified</b>	<b>2,107</b>	<b>1,999</b>	<b>366</b>

<sup>a</sup> ND - not detected

Table 2: HWR&IC Pilot-Scale Test Results<sup>a</sup>

Soil	Initial Concentration	300/5 <sup>b</sup>	300/9	400/5	400/9
A	2107	85.4	140.6	10.78/8.94 <sup>c</sup>	0.97
B	1999	69.4	22.0	7.31	0.50
C	366	nd <sup>d</sup>	79.8	nd	3.41

<sup>a</sup> PAHs in parts per million (ppm)

<sup>b</sup> Nominal soil temperature in °C/Time at temperature in minutes

<sup>c</sup> duplicate tests

<sup>d</sup> nd - no data

Table 3: CWM X\*TRAX Pilot-Scale Test Data  
Sandy Soil with PCBs

Compound	Feed (ppm)	Product (ppm)	% Removal
PCBs	1,480	8.7	99.4
1,2,4-Trichlorobenzene	2.9	ND	>99.9
Di-n-Butylphthalate	1.0	0.24	76.0
Bis(2-Ethylhexyl)phthalate	9.1	0.18	98.0

Table 4: CWM X\*TRAX Pilot-Scale Test Data  
Clay, Silt & Gravel with PCBs

Compound	Feed (ppm)	Product (ppm)	% Removal
TPH	1,400	34	97.6
PCBs (Arochlor 1254)	2,800	19	99.3
1,2,4-Trichlorobenzene	6.8	ND	>98.0
Di-N-Butylphthalate	6.9	0.18	97.4
Bis(2-Ethylhexyl)phthalate	4.7	ND	>97.2

Table 5: CWM X\*TRAX Pilot-Scale Test Data  
Surrogate Feed

Compound	Feed (ppm)	Product (ppm)	% Removal
Methyl Ethyl Ketone	100.9	< 0.1	>99.90
Tetrachloroethylene	91.0	0.015	99.98
Chlorobenzene	61.8	0.0065	99.98
Xylene	56.4	0.0028	99.99
1,4 Dichlorobenzene	78.4	0.0014	99.99
1,2 Dichlorobenzene	537.0	0.0741	99.99
Hexachlorobenzene	79.2	0.300	99.62

Table 6: RSI Pilot-Scale Test Results at  
Waukegan Harbor and Hudson River

Run Date	Temperature °F Gas	Soil	Feed (ppm)	Product (ppm)
7-19	1000	325	44	1.6
8-27	1400	325	109	1.0
8-29	1400	300	53	1.5
8-30	1500	350	37	3.2
9-04	1600	350	31	0.9
9-10	1450	400	38	1.5
9-11	1500	400	28	4.0
9-12	1600	300	27	1.4
3-12	1500	325	12.8	0.5
3-15	1450	275	12.9	0.5
3-26	1200	270	8.6	1.3
3-27	1500	275	8.6	1.3
4-18	1400	275	206	0.8

Table 7: NBCB Dioxin Treatment Study  
Test Runs

Parameter	R1	R2	R3	R4	R5
Feed Rate lb/hr	31	31	55	97	44
Residence Time minutes	40	40	19	10.5	24
Soil Temperature °F	1040	1040	1040	1040	860
Soil Processed lb	150	299	359	680	220
Total TCDD (ppb) feed	--	274	239	268	235
treated	--	0.23	0.11	0.61	0.75
Total TCDF (ppb) feed	--	12.2	10.2	12.7	10.8
treated	--	0.23	0.11	0.61	0.75
2,4,5-T (ppm) feed	93	15	37	200	80
treated	<0.2	0.11	<0.2	<0.2	<0.2
2,4-D (ppm) feed	0.37	0.81	0.58	17.0	1.4
treated	<0.2	0.079	<0.2	<0.2	<0.2

Note: (--) this data unreadable in source report.

# EFFECTIVENESS OF THE STABILIZATION/SOLIDIFICATION PROCESS IN CONTAINING METALS FROM RCRA ELECTROPLATING WASTES

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**Abstract:** Wastewater treatment sludges from electroplating operations are subject to the land disposal restrictions of the Resource Conservation and Recovery Act (RCRA). The final rule (August 17, 1988) requires stabilization with cement or equivalent binders for RCRA waste code F006. Samples from two electroplaters were stabilized with cement, lime/fly ash and kiln dust pozzolan materials. The Toxicity Characteristic Leaching Procedure was performed on the 28-day cured specimens of the three binders. The metals and total cyanide leachate data are presented.

**Keywords:** Stabilization, solidification, evaluation, metals, cyanide

## INTRODUCTION

The U.S. EPA's Risk Reduction Engineering Laboratory conducted a study of the stabilization/solidification (S/S) technology for metals binding to support the development of treatment standards for electroplating wastes. This paper presents the results of the S/S evaluations.

Stabilization/solidification involves the mixing of a waste (F006) with a binder material to enhance the physical and chemical properties of the waste. The binder is typically a cement, pozzolan, or thermoplastic. Stabilization produces a chemical reaction that, in most cases, converts inorganic material to its least soluble and most environmentally inert form. Solidification improves the handling and physical

characteristics of the material. The two terms are commonly used together, as both technologies are instrumental in immobilizing metals.

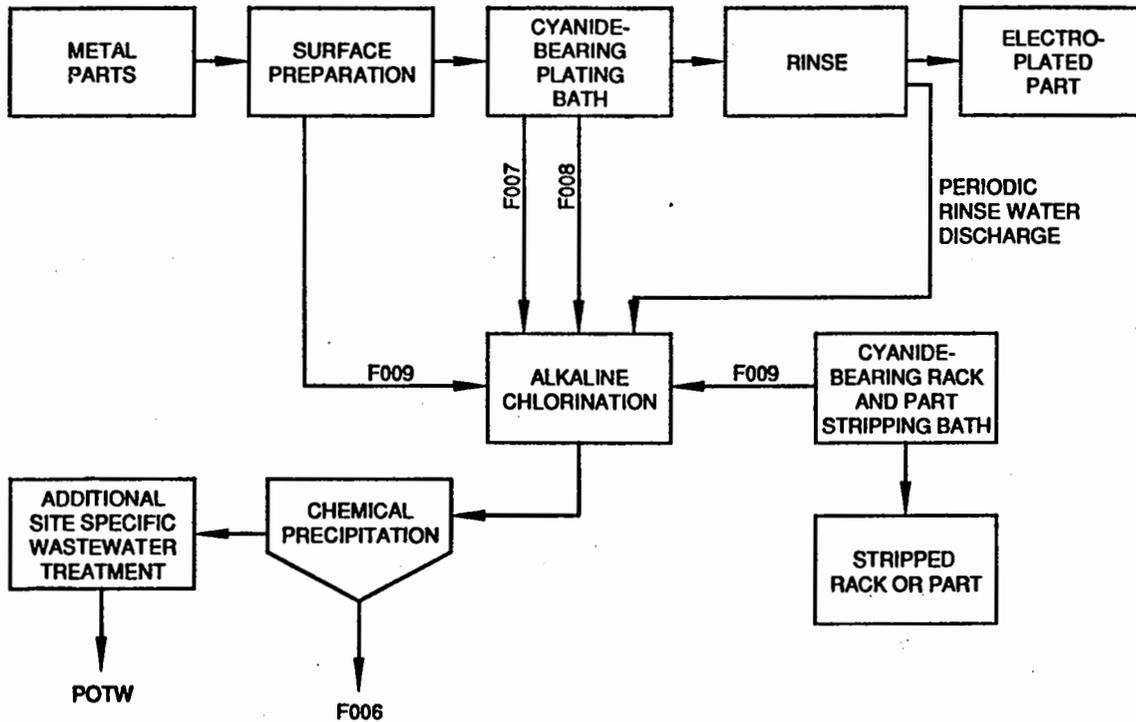
## **WASTE DESCRIPTION**

The term F006 is defined as wastewater treatment sludges from electroplating operations. Generation of F006 is depicted in Figure 1. Table 1 presents the standards promulgated for F006 on August 17, 1988.<sup>(1)</sup>

The F006 samples were obtained from a manufacturer of decorative hardware plated with brass, copper, zinc, nickel, and chrome (Facility A) and from a facility with barrel and rack lines dedicated to nickel-chromium, nickel-copper, cadmium, and chromium plating (Facility B). Both facilities use alkaline chlorination, chemical precipitation, and sludge dewatering for their electroplating wastes. The composition of Facility A's F006 was claimed to be confidential business information (CBI). The composition of Facility B's F006 is given in Table 2.

## **STABILIZATION/SOLIDIFICATION PROCESS**

The three binding agents used for the F006 S/S tests were Type 1 Portland cement, a 1:1 mixture of lime/fly ash, and kiln dust.<sup>(2)</sup> Analyses of the binders indicated the presence of chromium, lead, and nickel (Table 3). During bench-scale testing, different binder-to-waste ratios were used to stabilize/solidify the waste samples. (All S/S processes increase the volume of the final product for disposal). A screening test was performed to determine the appropriate amounts of water for hydration and the binder/waste ratios. The final binder/waste ratios used for the tests were 1.9 (cement),



F006 - WASTEWATER TREATMENT SLUDGES  
 F007 - SPENT CYANIDE PLATING BATH SOLUTIONS  
 F008 - PLATING BATH SLUDGES  
 F009 - SPENT STRIPPING AND CLEANING BATH SOLUTIONS

Figure 1. Hypothetical Cyanide-Bearing Electroplating Process.

**TABLE 1. TREATMENT STANDARDS, METAL-FINISHING  
SUBCATEGORY FOR F006 (NONWASTEWATERS)**

Constituent	Maximum for any single grab sample	
	Total composition, mg/kg	TCLP, mg/L
Cyanides (total)	590	a
Cyanides (amenable)	30	a
Cadmium	a	0.066
Chromium	a	5.2
Lead	a	0.51
Nickel	a	0.32
Silver	a	0.072

<sup>a</sup> Not applicable

Source - Reference 1

**TABLE 2. SUMMARY OF FACILITY B F006 METAL ANALYSES  
(mg/kg)**

Arsenic	0.62
Barium	6.9
Cadmium	39,900
Chromium (T)	4,840
Chromium (+6)	24
Copper	7,900
Iron	12,450
Lead	10
Nickel	11,650
Zinc	4,680

average of 6 tests

**TABLE 3. BINDER TCLP ANALYSES  
(µg/L)**

	Cadmium	Chromium	Lead	Nickel
Average Cement	<0.1	314	4	1.5
Average Kiln Dust	<0.1	58	38	2.6
Average Lime/Fly Ash	<0.1	26	7	1

average of 3 tests

Source - Reference 3

0.4/0.4 (lime/fly ash), and 0.7 (kiln dust). The selected ratios contained the lowest waste/binder ratios that exhibited a minimum strength of 50 psi.

After mixing, the 2-in.<sup>3</sup> test specimens were prepared and cured for 28 days at 23°C and 98 percent relative humidity. One set of samples from the Facility A waste was cured for just 24 hours to note any differences in leachability versus a 28-day cure. Facility B samples were tested after 28-day curing. Figure 2 presents a flow diagram of the S/S process used by the U.S. Army Corps of Engineers Waterways Experimental Station, Vicksburg, MS, to prepare the test samples for the EPA. A pass/fail compressive test value of 50 psi was used to select specimens for chemical analyses and leaching tests. All extractions were conducted in accordance with Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods, SW-846, third edition.<sup>(4)</sup>

## **METALS LEACHABILITY RESULTS**

Tables 4 and 5 present data for the Facility A tests and filter cake TCLP results at 24-hour and 28-day cures for the regulated metals. The TCLP were performed in triplicate for each binder, resulting in nine extractions. (The F006 total waste composition is claimed confidential by the generator and is not given.) The TCLP extracts for the F006-cement binder contained about 1 mg/L copper and 0.2 mg/L zinc for both the 24-hour and 28-day samples. The TCLP extracts for the F006-lime/fly ash and kiln dust binders had concentrations of these two metals approximately an order of magnitude higher. The nickel and chromium analyses showed low concentrations in the extracts of all three F006-binder combinations.

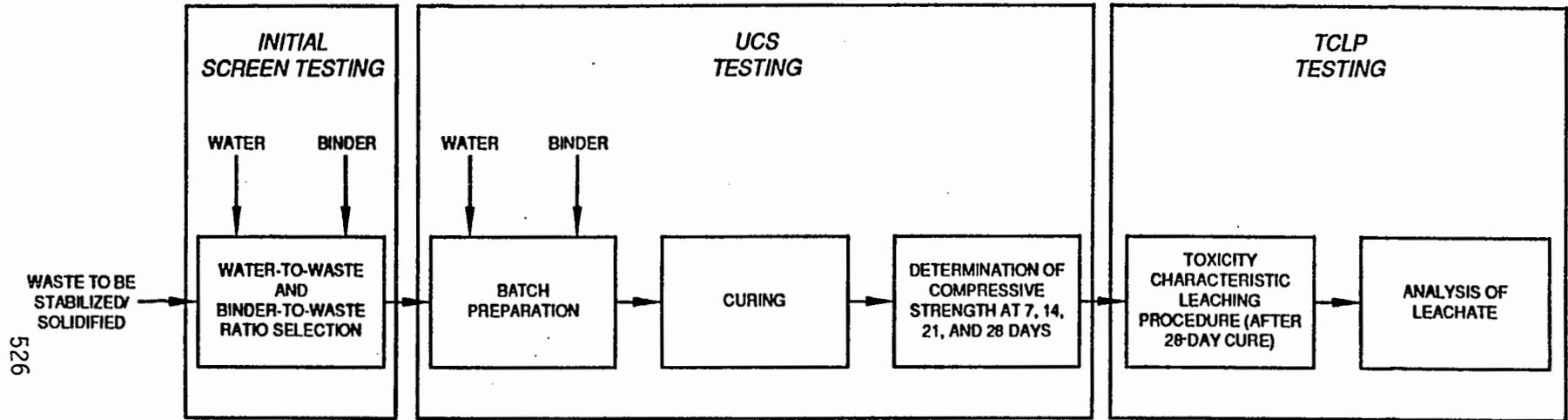


Figure 2. Flowchart for stabilization/solidification tests.

**TABLE 4. TCLP RESULTS OF UNTREATED F006 AND 24-HOUR  
F006 BINDER TESTS - FACILITY A  
(mg/L)**

	Untreated	Cement	Lime/fly ash	Kiln dust
Arsenic	0.006	0.002	0.002	0.002
Barium	<0.002	0.99	0.74	0.64
Cadmium	0.029	<0.004	<0.004	<0.004
Chromium (T)	0.055	0.15	0.02	0.03
Chromium (+6)	0.01	<0.25	0.03	0.11
Copper	135	0.96	7.08	6.53
Iron	<0.02	0.06	0.06	<0.02
Lead	<0.001	0.002	0.02	0.03
Nickel	26.8	<0.04	<0.04	<0.04
Zinc	244	0.17	3.18	2.88

Source - Reference 2

**TABLE 5. TCLP RESULTS OF 28-DAY  
F006 BINDER TESTS - FACILITY A  
(mg/L)**

Metal	Cement	Lime/Fly ash	Kiln dust
Arsenic	<0.002	<0.002	<0.002
Barium	0.91	0.6	0.42
Cadmium	<0.003	<0.003	<0.003
Chromium	0.2	0.084	0.12
Chromium (+6)	0.19	0.049	0.09
Copper	0.83	7.36	5.89
Iron	0.25	<0.02	<0.015
Lead	0.006	0.019	0.03
Nickel	<0.025	<0.04	<0.025
Zinc	0.2	2.63	3.13

Source - Reference 2

TABLE 6. TCLP RESULTS OF UNTREATED F006 AND  
28-DAY BINDER TESTS - FACILITY B  
(mg/L)

Metal	Untreated	Cement	Lime/fly ash	Kiln dust
Arsenic	0.002	<0.002	<0.002	<0.002
Barium	0.39	0.37	0.32	0.29
Cadmium	1298	0.28	0.08	64.2
Chromium (T)	0.66	0.44	0.28	0.07
Chromium (+6)	0.01	0.04	0.34	0.06
Copper	15	0.26	0.21	0.49
Iron	<0.01	1.0	0.14	<0.01
Lead	<0.001	<0.001	<0.001	<0.001
Nickel	255	<0.03	<0.03	8.78
Zinc	88	0.09	0.09	1.3

All silver results were less than the method detection limit and are not reported here.

Table 6 presents results of the analyses of Facility B's filter cake leachate and the TCLP extracts of the 28-day cured samples. With the kiln dust binder, extracts averaged about 64 mg/L cadmium, 0.06 mg/L hexavalent chromium, and 8.8 mg/L nickel. The cement binder extracts showed 0.28 mg/L cadmium, 0.04 hexavalent chromium, and nickel below the detection level (0.03 mg/L). The lime/fly ash binder extracts showed 0.08 mg/L cadmium and 0.34 mg/L hexavalent chromium; no nickel was detected in these extracts.

## **TOTAL CYANIDE RESULTS**

The total cyanide, CN(T), represents all cyanide species in the sample, including metal complexes but excluding cobalt, gold, and some platinum group metals. The CN(T) is determined by SW-846 Methods 9010 or 9012 (reflux mineral acid distillation).

Table 7 summarizes the cyanide data for F006 from both facilities. The average CN(T) in the untreated filter cake samples was approximately 722 mg/kg for Facility A and about 2400 mg/kg for Facility B. As a special test, the CN(T) was determined for the two unstabilized (untreated) wastes (before and after leaching) and for Facility A stabilized samples and the TCLP leachates. (Note: Total cyanide is regulated by content after stabilization, not by the TCLP tests.) Apparently, about half of the cyanide remained in the unstabilized F006 residue after leaching with TCLP extraction fluid No. 2 (pH =  $2.88 \pm 0.05$ ). CN(T) in two TCLP leachates was found to be below detection

limits. Under proper conditions, the low pH of the extraction fluid could have generated hydrogen cyanide. However, there was no qualitative evidence of hydrogen cyanide release during this study. The stabilized sample CN(T) values were not adjusted for dilution; however, there seems to be a "binder effect" with the lowest 28-day CN(T) result from the Facility A kiln dust matrix.

TABLE 7. SUMMARY OF F006 CYANIDE DATA

Analysis	Facility A	Facility B
Untreated F006 <sup>a</sup>		
Total waste analyses	722 mg/kg	2392 mg/kg
TCLP <sup>b</sup>	<0.02 mg/L	<0.04 mg/L
TCLP residue	396 mg/kg	1212 mg/kg
28-Day Cure		
Total Waste Analyses		
Cement <sup>c</sup>	535 mg/kg	NM <sup>d</sup>
Lime/fly ash <sup>e</sup>	234 mg/kg	
Kiln dust <sup>f</sup>	163 mg/kg	
TCLP		
Cement <sup>c</sup>	0.39 mg/L	NM
Lime/fly ash <sup>e</sup>	<0.02 mg/L	
Kiln dust <sup>f</sup>	<0.04 mg/L	

- <sup>a</sup> Moisture content, 72.9 percent, average
- <sup>b</sup> Extraction fluid No. 2 (pH = 2.88 ± 0.05)
- <sup>c</sup> 1.9 Binder/water (b:w)
- <sup>d</sup> NM - Not measured
- <sup>e</sup> 0.4/0.4 b:w
- <sup>f</sup> 0.7 b:w

## CONCLUSIONS

Nickel and cadmium were highest in the Facility B kiln dust leachate and failed the TCLP standard for these metals. The other two stabilized samples from Facility B also failed the TCLP for cadmium. The lime/fly ash binder gave the lowest leachable

cadmium and nickel values. All of the Facility A samples passed the TCLP for regulated metals. These results indicate a need for a cadmium recovery process at Facility B and proper binder selection for S/S.

Differences in the TCLP metals values due to the binders used (copper, zinc, chromium, nickel plating) for the 24-hour and 28-day S/S tests for Facility A were minimal; however, the cement binder was the more effective stabilizer for copper and zinc. The chromium and other metals detected in the binder materials had little effect on the final TCLP results. The binder selection may have an impact on the CN(T) results obtained after S/S treatment.

**Acknowledgment:** Phil Utrecht, PEI Associates, Inc., is acknowledged for his assistance in the preparation of this paper, and the Waterways Experimental Station is acknowledged for performance of the stabilization/solidification tests.

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FIELD ASSESSMENT OF AIR EMISSIONS FROM  
HAZARDOUS WASTE STABILIZATION OPERATIONS

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ABSTRACT

Millions of tons of hazardous waste are generated every year. One treatment method for hazardous waste is stabilization which creates a cement/waste mix that may be disposed of at a landfill. Since the waste is derived from a number of processes, a variety of volatile and semi-volatile organics may be present. Stabilization operations which mix and heat the waste increase the potential for the release of particulates and organics to the air. This paper presents the results of a comprehensive study that was performed for the EPA to quantify the release of volatile and semi-volatile organics as well as particulates from stabilization operations. The study included a field test of one stabilization operation in which material balance was used to calculate air releases.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

Hazardous waste stabilization is a process used by industry to stabilize or fix hazardous waste before it is disposed of on land. The sludge stabilization process involves fixing the waste with organic or inorganic agents. This fixation process mixes and heats the waste, possibly resulting in the vaporization of organics.

The U.S. Environmental Protection Agency (EPA) is currently collecting information to develop standards necessary for the control of air emissions from hazardous waste treatment, storage, and disposal facilities (TSDFs). The Office of Air Quality Planning and Standards (OAQPS) has identified stabilization facilities as a source of organic emissions at TSDFs. These field tests were conducted to aid in the development of standards for hazardous waste stabilization operations. The main objectives of this study were to:

- ° Characterize the fate of volatile and semi-volatile organics in the stabilization of hazardous waste;
- ° Quantify particulate emissions released during the stabilization process; and
- ° Quantify organic emissions released during the stabilization process.

This paper provides general information on the stabilization process, discusses the stabilization operations at one facility tested, and discusses the procedures and methods used to determine air emissions from the stabilization process.

## STABILIZATION METHODS

As mentioned earlier, the objective of hazardous waste stabilization is to stabilize hazardous wastes to allow for land disposal. Stabilization, also referred to as waste fixation, involves the addition of an organic or inorganic agent.

The vast majority of stabilization facilities operate on a batch system. After a certain amount of waste is received, it is stabilized and sent for disposal. Typically, waste is received in drums, trucks or rolloff boxes. It is emptied either into a mixing unit where stabilizing agents are added through the use of an auger type mechanism or into a holding pit. At some facilities, drum waste is removed from the drums and the drums are recycled. At other facilities, the drums are included with the waste to be stabilized. Both the mixing and holding areas may serve as premixing areas where mixing is performed with a backhoe to obtain a uniform waste feed. If a holding pit is used, once enough waste is received and mixed, it is sent to the mixing unit.

The mixing unit is usually a large concrete or steel bin, tank or mechanical mixing unit. The amount of agent added is determined by tests conducted on the waste feed. Inorganic (cement and pozzolans) or organic (asphalt and organic polymerization) stabilizing agents are added. Inorganic agents including portland cement, lime kiln dust and fly ash are the more common additives. Bench-scale tests have found the mixing process to be a major source

of volatile and semi-volatile organics.

After mixing, the cement/waste mix is allowed to cure for a period of approximately 24 hours either in the mixing unit or in a curing unit. Examples of curing areas are tanks and rolloff boxes. Since the waste may remain at elevated temperatures during curing, this point in the process may be a source of volatile emissions. The curing process is a minor source of volatile organic compounds according to bench-scale tests. After curing is complete, the cement/waste mix is sent for disposal to an on or off-site landfill. The waste is removed with a backhoe or through the use of a conveyor system and emptied into trucks for transport.

Particulate air emission control devices are most common at stabilization facilities. Some facilities may also utilize scrubbers or carbon adsorbers for volatile control.

#### STABILIZATION PROCESSES FOR ONE SELECTED FACILITY

Eight facilities across the country were visited to observe and review their sludge stabilization processes. The capacity and method of stabilization varied from site to site. The facility tested was selected because of the presence of a ventilation system, good testing conditions, and the broad spectrum of hazardous waste received.

The test facility has one stabilization unit with a total waste throughput of 20,000,000 gallons a year. After stabilization, the cement/waste mix is disposed of at a landfill. Any cement/waste mix not meeting established disposal criteria is recycled.

The process utilizes a series of enclosed mixers which blend the waste and stabilizing agent. The interior of the process building is vented to either activated carbon adsorbers for control of organic emissions or to both a venturi type (Wet Air Tumbler) scrubber for particulate control followed by the activated carbon adsorber.

The flow diagram for the test facility's hazardous waste stabilization process is shown in Figure 1. The waste is received at the site as bulk liquid in tankers; bulk sludge in vacuum trucks; bulk solids in rolloffs or dump trucks; and liquid, sludge or solids in drums. All of the solids, liquids, and sludges are put into a 10,000 gallon open tank, called the Non-Pumpables tank.

The Non-Pumpables tank is a large 10,000 gallon open tank. The wastes exit the Non-Pumpables tank through an auger/grinder pump which is attached to the end of a backhoe arm. As the backhoe arm moves around the tank, the screw auger sends the waste to the grinder pumps which both grinds the wastes and pumps it through a flexible hose which runs along the arm of the backhoe to a small surge tank. The auger can also be used to circulate the waste in the tank while the pump is not operating.

The waste is pumped from the surge tank up to the B-Hopper which acts as a surge protector for the #2 Mixer. The stabilizing agents, cement kiln dust and lime kiln dust, are added to the waste from the B-Hopper in the #2 Mixer

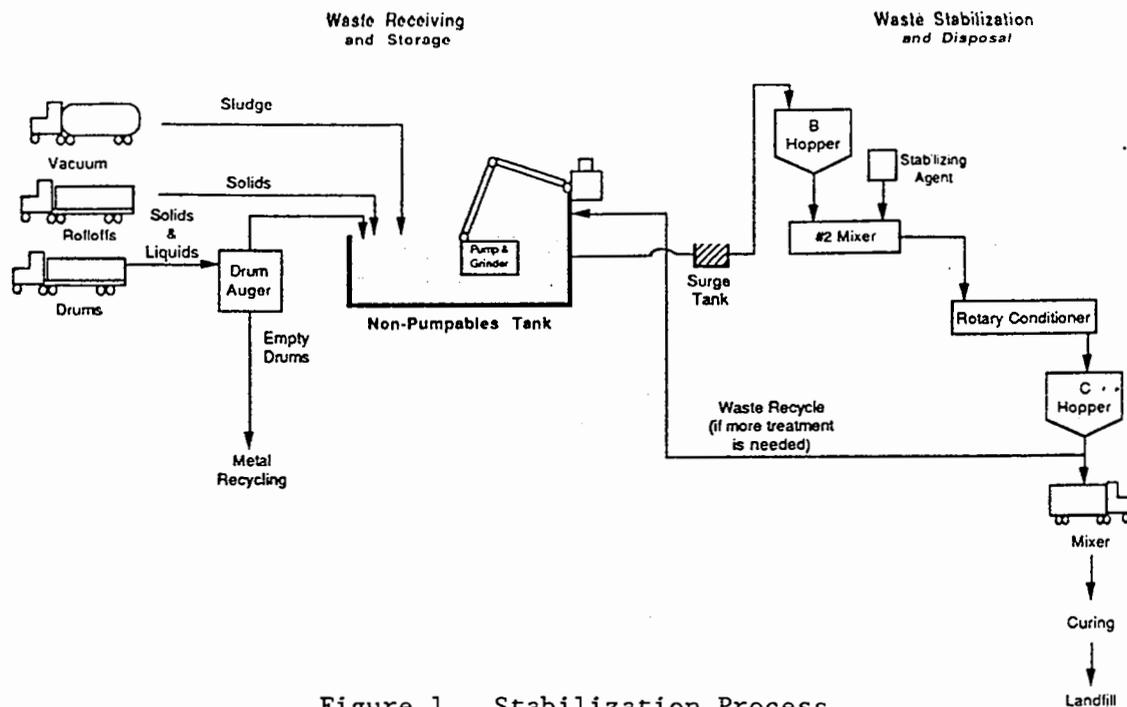


Figure 1. Stabilization Process.

which is a pug mill.

The cement/waste mix leaves the #2 Mixer as a pumpable slurry and is fed directly to the Rotary Conditioner, a rotating drum approximately 10 feet in diameter and 60 feet long. The Rotary Conditioner completes the blending operation. The waste leaves the Rotary Conditioner and drops into the C-Hopper. The cement/waste mix goes from the C-Hopper to cement mixer trucks via a screw auger and pump. The screw auger feeds the cement/waste mix from the C-Hopper to the pump and the pump moves the cement/waste mix to a chute which hangs over the cement mixer trucks. The cement mixer trucks empty the cement/waste mix into large roll-off boxes located outside where it is allowed to cure. Once curing is complete, the stabilized waste is removed from the roll-off boxes and trucked to a landfill for disposal.

All of the process equipment and the building in which processing takes place is vented to one of two air handling systems which are identified by their capacity, 20,000 cfm and 40,000 cfm. The 20,000 cfm system vents the air from the drum handling area of the building. In this area, dust is not a problem so this vents directly into a carbon adsorption system. The remainder of the areas are vented through the 40,000 cfm system. These sources produce dust as well as organic vapors, so this stream is first sent through a venturi scrubber, followed by an 8 foot thick, 8 foot diameter mist eliminator, an air preheater, a disposable prefilter, and finally two parallel carbon adsorption systems.

#### TESTING METHODS AND RESULTS

As discussed previously, the objectives of the field tests were to determine the percent of volatile and semi-volatile organics emitted from the waste and to estimate the particulate air emissions during the stabilization process. To meet these objectives tests were performed on the waste feed, exhaust air and cement/waste mix. Samples of the waste feed were taken from the

following locations: the surge tank, the chute for the cement/waste mix to the cement mixer truck, the exhaust air system from the B-hopper vent, and the exhaust air system from the #2 mixer/rotary conditioner vent. These samples were collected and analyzed for volatile and semi-volatile organic compound concentrations. Figure 2 shows the sample locations at the test facility.

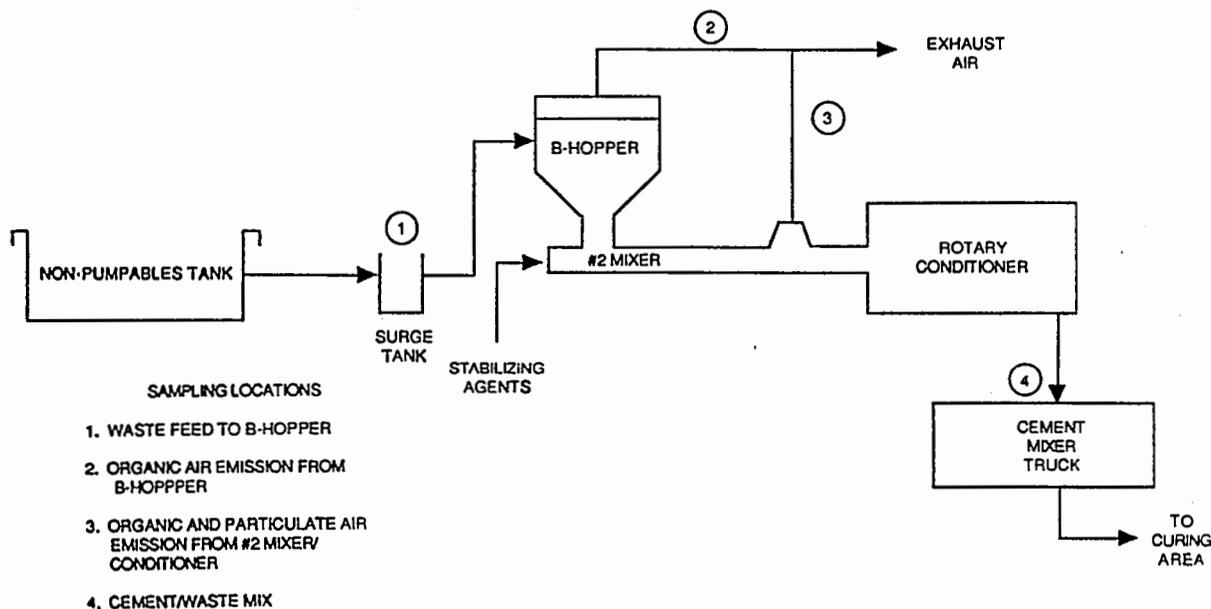


Figure 2. Sampling Locations.

Waste and Cement/Waste Mix Sampling and Analysis

Three 3-hour sampling runs were conducted over a period of three days. Samples were collected and flow rates were measured at half-hour intervals during each run. Flow rates for the inlet and outlet streams were measured by reading flow meters and/or collection a known quantity of material for a fixed period of time. Table 1 shows the measured feed rates for the field test.

TABLE 1. MASS FLOWS DURING THE FIELD TEST, lb/h

Run	Waste feed (lb/h)	Cement/waste mix (lb/h)
1	24,054	39,798
2	17,694	32,214
3	20,466	39,348
Avg.	20,738	37,120
Std. Dev.	3,189	4,255

Samples were collected as follows:

- waste feed - dipping a bucket into the surge tank located between the Non-Pumpables tank and the B-Hopper.
- cement/waste mix - lowering a bucket into the chute feeding the cement mixer trucks. The cement/waste mix samples were collected 20 minutes after the waste feed samples to allow for the estimated Rotary Conditioner residence time.

For volatile and semi-volatile analysis of the waste feed, four 40-ml VOA vials were collected. Two vials were reserved for volatile analysis, and two were reserved for semi-volatile analysis. Approximately four drops of HCl were added to each vial. The vials were filled completely to eliminate headspace and stored in an ice-chilled cooler for transport. The vials for volatile analyses were analyzed separately. The vials for semi-volatile analyses were composited in the laboratory and aliquots taken for analysis.

For volatile and semi-volatile organic analyses of the cement/waste mix, duplicate grab bag samples were collected at half hour intervals. Each 40-ml VOA vial was weighed empty, then partially filled with methanol, and reweighed. Approximately 20 grams of cement/waste mix was added to the vial and the vial was weighed to determine the amount of sample. The vial was then filled completely with methanol, weighed and shaken to disperse the solids. In the laboratory, each sample was analyzed separately according to Methods 5030 and 8240 (GC/MS).

#### Exhaust Air Sampling and Analysis

Sampling of the air exhaust system was performed by accessing a platform located at the vent from the chute between the #2 Mixer and Rotary Conditioner

Volatile organic content of the exhaust air was measured following the guidelines of EPA Method 18 (40 CFR 60, Appendix A, July 1989). Duplicate samples were collected at sites 2 and 3. At both sites, the sampling trains consisted of a Teflon line into the stack and two 1-gram sized coconut shell charcoal tubes in series. At Site 3 (#2 Mixer/Conditioner vent), the sample volume was measured with a dry gas meter measuring 1 liter/revolution with  $\pm 2$  percent accuracy. At Site 2 (B-Hopper vent), calibrated personnel sampling pumps were used. The pump flow rate was measured before and after each test with a bubble buret.

Samples at sites 2 and 3 were collected over a three-hour period at a rate of about 200 ml/minute. After the test, each charcoal tube was capped and stored in a plastic bag on ice. The front and back charcoal tubes were analyzed separately to determine the extent of sample breakthrough. Each tube was desorbed with 2 ml of carbon disulfide. Because volatile components such as acetone and methylene chloride are major constituents in this waste, analyses were conducted by GC/FID instead of GC/MS.

Gaseous semi-volatile organics in the exhaust air were also measured by EPA Method 18. The sampling trains were identical to the volatile organic train except the charcoal tubes were replaced with 3.5-gram capacity XAD-2 tubes. Duplicate samples were collected over three-hour periods at a rate of

1 liter/minute. EPA Method 8270 was used to analyze the XAD-2 tubes for HSL semi-volatile organics. Method 8270 uses methylene chloride to soxhlet extract the XAD-2 tubes. This sampling method was selected because it is equivalent to the procedures used at the laboratory bench study. However, the method could be biased by semi-volatile organics adsorbed into the particulate matter. For this reason, a second set of samples was collected at Site 3 by the standard EPA Modified Method 5. The XAD-2 tubes were prepared by PEI.

Flow rate composition was determined using EPA Methods 1 through 4 at Sites 2 and 3. Method 1 is used to select the sample points. Method 2 is used to determine the gas velocity and temperature. Method 3 is used to determine the oxygen content of the stream. Method 4 is used to determine the moisture content of the stream. This information is needed to calculate exhaust air flow rates.

### Mass Flow Rate and Emission Results

Tables 2 and 3 show the mass flow rates of the volatile and semi-volatile organics, respectively.

TABLE 2. SUMMARY OF VOLATILE ORGANIC COMPOUND FEED RATES

Compound	Waste Feed Compound Feed Rate, lb/h			Cement/Waste Mix Compound Feed Rate, lb/h		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
	Methylene chloride	0.8765	0.2678	1.342	5.4854	3.4301
Acetone	0.4226	0.5981	0.1729	0.4039	0.2545	0.1472
2-Butanone	0.3099	0.3214	1.1432	0.3271	0.3695	0.4120
4-Methyl 2-pentanone	0.1684	0.0544	0.2941	0.0955	0.0522	0.1094
Toluene	0.9866	2.5214	2.0411	1.9931	2.0714	1.7443
Ethylbenzene	0.4199	3.5696	1.706	1.0634	2.8719	1.7270
Xylenes	2.5483	17.782	8.1659	5.3735	14.661	9.0390
Benzene	0.0145	0.2011	0.0882	0.0135	0.0680	0.0523
1,1,1-Trichloroethane	0.1391	0.1094	2.7161	0.2491	0.1340	2.0815
Trichloroethene	0.2065	0.3206	0.6417	0.5281	0.2297	0.5103

TABLE 3. SUMMARY OF SEMI-VOLATILE ORGANIC COMPOUND FEED RATES

Compound	Waste Feed Compound feed rate, lb/h			Cement/Waste Mix Compound Feed Rate, lb/h		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
	Phenol	3.127	17.694	4.2979	0.109	0.3772
Naphthalene	--	0.6724	3.2746	--	0.0812	0.4128
2-Methylnaphthalene	0.1443	0.5308	2.2513	--	0.0573	0.3939
1,2,4-Trichlorobenzene	--	--	0.8596	--	--	0.0952

Volatile and semi-volatile organic emission factors are shown in Tables 4 and 5. The emission factor for each chemical is the ratio of the mass flow rate out the stack to the mass flow rate in the feed. This represents the fraction of each organic that would be released to the air.

TABLE 4. EMISSION FACTORS FOR VOLATILE ORGANIC COMPOUNDS

Compound	Compound feed rate, lb/h			Air emission rate, lb/h			Air emission factor, lb/lb of feed			
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Overall average
	Methylene chloride	0.8765	0.2678	1.342	2.544	4.016	34.082	2.902	14.996	25.463
Acetone	0.4226	0.5981	0.1729	0.087	0.254	0.406	0.206	0.425	2.348	2.979
2-Butanone	0.3099	0.3214	1.1432	0.087	0.248	2.948	0.281	0.772	2.579	1.211
4-Methyl 2-pentanone	0.1684	0.0544	0.2941	0.204	0.230	2.827	1.211	4.228	9.612	5.017
Toluene	0.9866	2.5214	2.0411	0.591	0.986	1.212	0.599	0.391	0.594	0.528
Ethylbenzene	0.4199	3.5696	1.706	0.212	1.049	0.444	0.505	0.294	0.260	0.353
Xylenes	2.5483	17.782	8.1659	0.944	4.571	1.640	0.384	0.257	0.201	0.281
Benzene	0.0145	0.2011	0.0882	0.099	0.120	1.731	6.828	0.597	19.626	9.017
1,1,1-Trichloroethane	0.1391	0.1094	2.7161	0.240	0.348	2.965	1.725	3.181	1.092	1.999
Trichloroethene	0.2065	0.3206	0.6417	0.286	0.330	3.789	1.385	1.029	5.905	2.773

TABLE 5. EMISSION FACTORS FOR SEMI-VOLATILE ORGANIC COMPOUNDS

Compound	Compound feed rate, lb/h			Air emission rate, lb/h			Air emission factor, lb/lb of feed		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
	Phenol	3.127	17.694	4.2979	3.9E-04	5.6E-04	3.3E-04	1.2E-04	3.2E-05
Naphthalene	--	0.6724	3.2746	3.5E-03	4.2E-03	1.8E-02	--	6.2E-03	5.5E-03
2-Methylnaphthalene	0.1443	0.5308	2.2513	1.0E-03	7.7E-04	2.8E-03	6.9E-03	1.5E-03	1.2E-03
1,2,4-Trichlorobenzene	--	--	0.8596	--	--	4.1E-03	--	--	4.8E-03

Total volatile organic concentrations were measured using a continuous-flame ionization analyzer (FIA) and the procedures of EPA Method 25A at Sites 2 and 3. The sampling system consisted of a heated Teflon sample line maintained at 280°F and a Beckman Model 402 FIA. The analyzer was calibrated with gas standards of methane in hydrocarbon-free air. The total organic content of the sample was compared with the methane response factor and was then reported as ppm methane equivalent. This procedure does not yield an exact measurement of the total organic carbon due to the fact that the carbon response on an FIA will vary depending on the molecular structure. Table 6 summarizes the results of the FIA and OVA analyses. There is little difference between the total VOC measured by each method.

TABLE 6. COMPARISON OF TOTAL VOC EMISSIONS MEASURED BY FIA TO TOTAL SPECIFIC COMPOUND EMISSIONS BY METHOD 18

Run No.	Site 2-B Hopper Vent		Site 3-Conditioner/Mixer Vent	
	Total VOC by FIA, lb/h(1)	Total VOC by Method 18, lb/h	Total VOC by FIA, lb/h(1)	Total VOC by Method 18, lb/h
1	0.81	0.88	5.26	4.41
2	1.46	1.66	11.70	10.49
3	3.31	4.54	43.16	47.60

(1)Pounds per hour as Methane.

Particulate emissions were measured at Site 3 (#2 Mixer/Conditioner) using EPA Modified Method 5 as described in Method 0100 of EPA SW846. The Modified Method 5 sample train was also used at Site 3 to sample for semi-volatile organics. The filter and the probe rinse were analyzed for particulate. One three-hour Modified Method 5 sample was collected during each run. Particulate emissions were sampled only from the #2 Mixer/Conditioner vent. The particulate emissions were sampled using an EPA Modified Method 5 as described in Method 0010 of EPA SW846. The results of the particulate emission sampling are shown in Table 7.

TABLE 7. UNCONTROLLED PARTICULATE EMISSIONS FROM SITE 3 - CONDITIONER/MIXER VENT

Run No.	Particulate concentration, gr/dscf(1)	Particulate emission rate, lb/h
1	0.064	1.20
2	0.210	4.84
3	0.065	1.42
Average	0.113	2.49

(1)Grains per dry standard cubic foot at 68 F, 29.92 in. Hg, and zero percent moisture.

#### Quality Assurance/Quality Control

Quality assurance and quality control procedures were employed during the laboratory analysis of all samples obtained during this project. All samples of the exhaust air were collected in duplicate and desorption efficiency for each compound was determined. The quality assurance objectives for precision ( $\pm 10$  percent) and accuracy ( $\pm 30$  percent) were met for all compounds. Semi-volatile samples were spiked with the surrogates and duplicate samples were collected by Method 18. The relative standard deviation between duplicate semi-volatile samples found above detection limits met the QA objective of  $\pm 30$  percent with few exceptions. The volatile compound QC samples consisted of matrix spikes and method blanks. The QA objective for precision ( $\pm 30$  percent) and accuracy as percent recovery of matrix spikes (40 to 160 percent) were met for all compounds.

## DISCUSSION OF RESULTS

Air emission results obtained in this study indicate the extent of air emissions from the mixing process. For both volatile and semi-volatile compounds, the precision for the air sampling method as measured by the relative percent difference between duplicate samples were quite good. Also, the accuracy of the air stream measurements as measured by recovery of target compounds was good. In addition, a comparison of results obtained by Method 18 and Method 25A (Table 6) supports the accuracy and consistency of the air emissions data. It should be noted that liquid wastes added to the sludge in the Non-Pumpables tank were highly variable during this study. Thus, cross-averaging the runs is not necessarily meaningful.

Material balance closure was not attainable for all compounds, especially semi-volatile compounds. The method for volatile and semi-volatile organic analyses for the cement/waste mix was untried and the relative accuracy is unknown. The major factor influencing the mass balance was the inability to accurately test the cement/waste mix samples. Analytical methods for testing cement are not established. In addition, the analytical methods used in sampling the exhaust air streams were much more precise than those available for analyzing the waste feed and cement/waste mix. As a result, a much higher degree of accuracy and certainty was achieved from the air sampling, creating higher effluent rates than feed rates.

The semi-volatile compounds listed in Tables 3 and 5 are those measured above the detection limits in one or more exhaust air runs. Both tables 4 and 5 show the results of the tests in terms of pounds of volatile organics emitted to the air per pound of feed sent to the stabilization process. The emission factors for some of the volatile organics were greater than one. This is not a realistic occurrence since the emission factor represents the ratio of the compound emission rate to the compound feed rate. A value less than or equal to one is expected as the amount of a particular compound exiting the system cannot be greater than the amount entering the system. In particular, emissions factors for methylene chloride, 4-methyl 2-pentanone and benzene were significantly greater than one. The inconsistent emissions factors are due to the following: 1) variability in waste stream composition, 2) the methods used to analyze the waste feed and the cement/waste mix were not as accurate as those used to analyzed the exhaust air stream, 3) fluctuations in the flow rate of the waste feed and cement/waste mix.

During stabilization operations, organics may be released to the air. Test results showed a large fraction of the volatile organic compounds in the hazardous waste stabilized are emitted into the air during the mixing stages. In addition, particulate emissions measured using EPA Modified Method 5 were an average of 2.49 lb/h over all three runs. Finally, the organic vapor analyzer showed a mass flow rate of total volatile organic hydrocarbons of 21.9 lb/h averaged over all three runs. Based on an average of 20,738 pounds per hour of waste was fed to the system, 0.11 percent over three runs, by weight, of the feed is emitted to the air.

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ASSESSMENT OF THE PARAMETERS AFFECTING THE MEASUREMENT OF  
HYDRAULIC CONDUCTIVITY FOR SOLIDIFIED/STABILIZED WASTES

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ABSTRACT

A series of experiments conducted at the Alberta Environmental Centre examined the variation in hydraulic conductivity (K) within and among three matrices formed by steel mill baghouse dust treated with 8%, 9% and 10% Normal Portland Cement at a water/cement ratio of 1:1. Within the 8% and 9% matrices, test gradient (i) and back pressure (P) were combined into 3 x 3 factorial treatments.

A permeant-matrix interaction was indicated by K decreasing with time at a rate which increased with higher cement contents. After hydraulic conductivity testing, the samples were examined by scanning electron microscopy and energy dispersive x-ray analysis. A cement hydration product, identified as ettringite had formed in the solidified/stabilized waste pores. This product may reduce hydraulic conductivity by two orders of magnitude by restricting conducting pores. Four to seven weeks of testing were required before an acceptable equilibrium had been reached and statistical comparisons among the i x P treatments could be made. Within each matrix, gradient was statistically the most significant parameter accounting for 60% of the variation in results. The overall mean hydraulic conductivity was significantly greater for the eight percent matrix ( $10 \pm 5 \times 10^{-6} \text{ cm}\cdot\text{sec}^{-1}$ ) compared to the nine percent matrix ( $0.06 \pm 0.03 \times 10^{-6} \text{ cm}\cdot\text{sec}^{-1}$ ) ( $p \leq 0.01$ ). Therefore, temporal effects, gradient and cement content were identified as important factors affecting hydraulic conductivity measurements and have implications for regulatory tests. Bulk density was a useful quality control criterion for minimizing sampling variance within each matrix.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## ASSESSMENT OF THE PARAMETERS AFFECTING THE MEASUREMENT OF HYDRAULIC CONDUCTIVITY FOR SOLIDIFIED/STABILIZED WASTES

### INTRODUCTION

Solidification and stabilization (SS) technologies are often used to treat hazardous wastes to reduce the environmental impact of their disposal. Solidification removes free water, usually by the hydration reactions of lime or cementitious materials, producing a monolithic solid with reduced surface area. Stabilization with cementitious materials reduces the solubility of wastes by the alkaline precipitation of metal hydroxides or metal incorporation into the hydration products of cement.

The long term behaviour of these treated wastes is the subject of much concern. Depending on the disposal scenario, treated wastes are eventually subject to leaching by ground water, precipitation, or leachate. If the treated waste is relatively permeable, leachant flow will be through the bulk of the SS matrix rather than being confined to the external surface area. Thus, a major benefit of SS treatment, the reduction of surface area available for leaching, is compromised.

The flow of liquid through a porous medium is described by Darcy's Law. The liquid superficial velocity (Flowrate/Area) per unit gradient is defined as hydraulic conductivity, which is a function of the properties of the medium and the liquid. Gradient is defined as the headloss which occurs over the sample (cm of H<sub>2</sub>O) divided by the sample length (cm). Darcy's Law may be written as:

$$K = \frac{Q}{iA}$$

where K is hydraulic conductivity (cm.sec<sup>-1</sup>), Q is flow rate (cm<sup>3</sup>.sec<sup>-1</sup>), i is gradient (dimensionless) and A is cross-sectional area (cm<sup>2</sup>).

Permeability, a property of the medium alone, is related to hydraulic conductivity by the following relationship:

$$\kappa = \frac{K\mu}{\rho g}$$

where  $\kappa$  is permeability ( $\text{cm}^2$ ),  $\mu$  is absolute viscosity of the liquid ( $\text{g}\cdot\text{cm}^{-1}\cdot\text{sec}^{-1}$ ),  $\rho$  is density of the liquid ( $\text{g}\cdot\text{cm}^{-3}$ ) and  $g$  is acceleration of gravity ( $998 \text{ cm}\cdot\text{sec}^{-2}$ ).

When there is no medium-liquid interaction, permeability is an intrinsic and useful property of a medium. The flow rates of different liquids through a medium can be readily predicted from its permeability and the properties of the liquids. However, when there are changes in liquid properties, due to dissolution and in the internal structure of the medium, as shown in this paper, the meaning of permeability becomes obscure. Since it is the flow rate of aqueous permeant through SS waste which is of environmental interest, hydraulic conductivity is the proper terminology and is used herein.

The literature available on hydraulic conductivity measurement with environmental implications deals predominantly with clay and soil liners. Researchers are interested in the effects of permeants, specifically inorganic salt solutions (1), organic fluids (2) and landfill leachates (3). Test parameters such as saturation (4), temporal effects (5, 6) and gradient (6, 7) have been studied. Parker et al. (5) found that the hydraulic conductivity of fly ash-stabilized soils decreased over time possibly due to fly ash-soil interaction. Carpenter and Stephenson (6) and Edil and Erikson (7) both noted that hydraulic conductivity declined for clays as the gradient was increased when flexible wall permeameter cells were used.

Bryant and Bodocsi (8) collected historical data on hydraulic conductivity measurements for clay liners and analyzed them for the effects of sample variation, preparation, equilibration and gradient, among other effects. They noted many confounding effects, and suggested that suitable experimental designs should be chosen to properly estimate parametric effects. Longer test periods and statistical approaches to determine equilibrium, as indicated by stable hydraulic conductivity, were suggested. Soil hydraulic conductivity was found to be very sensitive to preparation technique. Some results showing decreasing hydraulic conductivity were explained by sample consolidation resulting from increased gradients.

Pierce et al. (9), who conducted ruggedness tests using both rigid wall and triaxial cell permeameters, found that water content, lift thickness and back pressure had the greatest effect on the measured hydraulic conductivity of a clay liner material. The first two factors pertain to sample preparation while the third is an instrument measurement parameter. Gradient was not found to be significant at relatively high levels ( $i = 100, 200$ ), typical of laboratory tests. The hydraulic conductivity results exhibited large variability. Thus, inter-laboratory results could exhibit large variation due to individual laboratories performing hydraulic conductivity tests at different levels of these sensitive parameters.

Stegemann and Cote (10) provided comprehensive information on the results of an inter-laboratory study evaluating test methods for SS treated wastes. Commercially available SS treatment processes provided hydraulic conductivities between  $3 \times 10^{-6}$  and  $7 \times 10^{-10}$  cm.sec<sup>-1</sup>. The inter-laboratory variance was too large to determine differences between individual products.

The work done on clay liners and soils suggests that if hydraulic conductivity measurement is to be used as a regulatory test for SS wastes, several factors should be studied: sample preparation, temporal effects, or time to equilibration, and the instrument measurement parameters of gradient and back pressure. These factors may affect reproducibility in terms of intra and inter-laboratory variance. Experiments should also be conducted across the range of hydraulic conductivities typical of SS wastes. The effects of gradient and back pressure on measured hydraulic conductivity may also provide the bases for evaluating the potential of laboratory tests as predictors of field results. Thus, experiments should include trials at low levels of gradient and back pressure approximating field conditions.

This study is necessary as SS wastes behave differently than clay liners and soils during hydraulic conductivity measurement due to their higher compressive strength and water-reactive cementitious matrix. This paper reports the results of experiments carried out at the Alberta Environmental Centre which were designed to address the possible effects of: gradient, back pressure (the outlet pressure used to ensure liquid saturation at a given gradient), time and matrix.

## MATERIALS AND METHODS

### SAMPLE PREPARATION

Samples for hydraulic conductivity measurement were prepared from steelmill baghouse dust, 16-30 mesh silica sand (Badger), ASTM Type 1 Portland Cement (Canada Cement LaFarge) and tap water. The sample formulations, shown in Table 1, were chosen to give a range of hydraulic conductivities typical of SS wastes ( $10^{-6}$  to  $10^{-9}$  cm.sec<sup>-1</sup>).

**TABLE 1. HYDRAULIC CONDUCTIVITY SAMPLE FORMULATIONS\***

Matrix	Steelmill Foundry Dust	Silica Sand	Type 1 Portland Cement	Water
8%	42.0	42.0	8.0	8.0
9%	41.0	41.0	9.0	9.0
10%	40.0	40.0	10.0	10.0

\* Sample formulations are given in weight percent.

Samples were compacted and bulk densities measured according to ASTM D558-82 (11), modified for sample size to ensure similar compaction energies. Samples were prepared in plastic molds 7.62 cm (diameter) x 15.2 cm (length) and cured for a minimum of 28 days at ambient temperature and a minimum relative humidity of 95%.

Samples were saturated in the triaxial cell prior to hydraulic conductivity testing by evacuating with a vacuum pump, isolating the sample, and allowing permeant flow from the inlet to restore ambient pressure.

### HYDRAULIC CONDUCTIVITY

Cured samples were tested for hydraulic conductivity by a constant head method based on USEPA SW 846 Method 9100 (12). Samples were tested concurrently on three Geotest Model No. S5425 permeameters (Figure 1). Each permeameter consisted of a triaxial sample cell with a flexible membrane confined at a pressure 21 kPa higher than the inlet pressure. The permeant inlet and outlet interfaces utilized a piston and linear transducer calibrated for volume and accurate to  $\pm 0.01$  ml across the interface volume of 50 ml. Data collected concurrently by the data loggers were downloaded to a computer for calculating hydraulic conductivities.

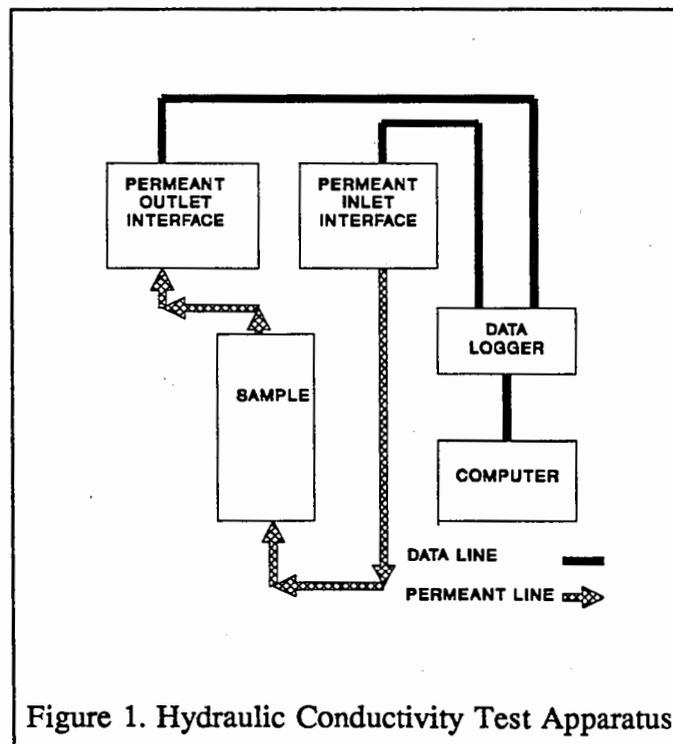


Figure 1. Hydraulic Conductivity Test Apparatus

## ELECTRON MICROSCOPY

Electron microscopical analyses were performed on a Hitachi S510 scanning electron microscope (SEM), a Hitachi X-650 (SEM) with energy dispersive x-ray spectrometer and a Hitachi H-600 scanning transmission electron microscope (STEM) equipped with a Kevex Be window x-ray detector.

## DETERMINATION OF HYDRAULIC CONDUCTIVITY EQUILIBRIUM

Simple, linear regression was used to identify the time ( $x = \text{day} = \text{independent variable}$ ) when changes in hydraulic conductivity ( $y = K \cdot 10^6 = \text{dependent variable}$ ) had attained sufficient stable equilibrium that the regression coefficient, or slope, was not different than zero, as suggested by Pierce and Witter (13).

Equilibria were reached by 59, 34 and 27 days for 8, 9 and 10 percent matrices respectively; the null hypothesis, that the estimated slope equalled zero, could not be rejected for any of the three matrices with a probability of Type I error less than 0.13.

## EXPERIMENTAL DESIGN

After equilibrium had been reached as indicated above, gradient and back pressure were varied and treated as independent continuous variables at three levels in a completely randomized 3 x 3 factorial design (see Table 2). Gradient levels corresponded to pressures of 10 kPa to 340 kPa. Two independent experiments were performed at 8%, and 9% matrix to provide a range of hydraulic conductivities. Second-degree polynomial coefficients were calculated using response surface regression (SAS 1988 Release 6.03 (14)) to model the response of hydraulic conductivity to varying levels of gradient and back pressure.

TABLE 2. TEST PARAMETERS AND LEVELS\*

Parameter	Level		
	-1	0	+1
Gradient	8	116	227
Back Pressure (kPa)	14	69	124

\*Performed at 8%, and 9% matrix

## RESULTS AND DISCUSSION

### SAMPLE PREPARATION

The samples had the consistency of soil-cement and thus were compacted with standard soil-cement procedures (11). The sample bulk densities are shown in Table 3. The percent relative standard deviation ranges from 0.431% to 0.924%.

TABLE 3. SAMPLE BULK DENSITIES

Matrix	8%	9%	10%
n <sup>+</sup>	6	10	6
Bulk Density (g.cm <sup>-3</sup> )			
Mean	2.270	2.327	2.390
S.D.	0.0137	0.0215	0.0103
RSD (%)	0.604	0.924	0.431

<sup>+</sup>n is the number of samples

Bulk density is a function of gross sample porosity and has been implicated as a source of variance in hydraulic conductivity measurements. The degree of compaction affects the measured permeability of clayey silt (15). Stegemann and Cote (10) felt that sample differences were a major source of variation in their hydraulic conductivity study.

Error introduced by weighing out reagents and sample mold variation was estimated to be 0.42%. Thus, a quality assurance criterion was instituted which rejected all samples with bulk densities not within  $\pm 0.5\%$  of the sample mean. By instituting strict quality control for sample preparation, a potential source of within matrix sample variation is reduced.

### TEMPORAL EFFECTS DURING EQUILIBRATION

Hydraulic conductivity measurements were recorded when inflow and outflow rates were determined to be equal (within 5%). The results summarized in Figure 2 show the temporal effects over 80 days of testing at constant gradient and back pressure. Also shown are the predicted hydraulic conductivities derived from a nonlinear regression. Hydraulic conductivity decreased by nearly two orders of magnitude for the highest cement content sample.

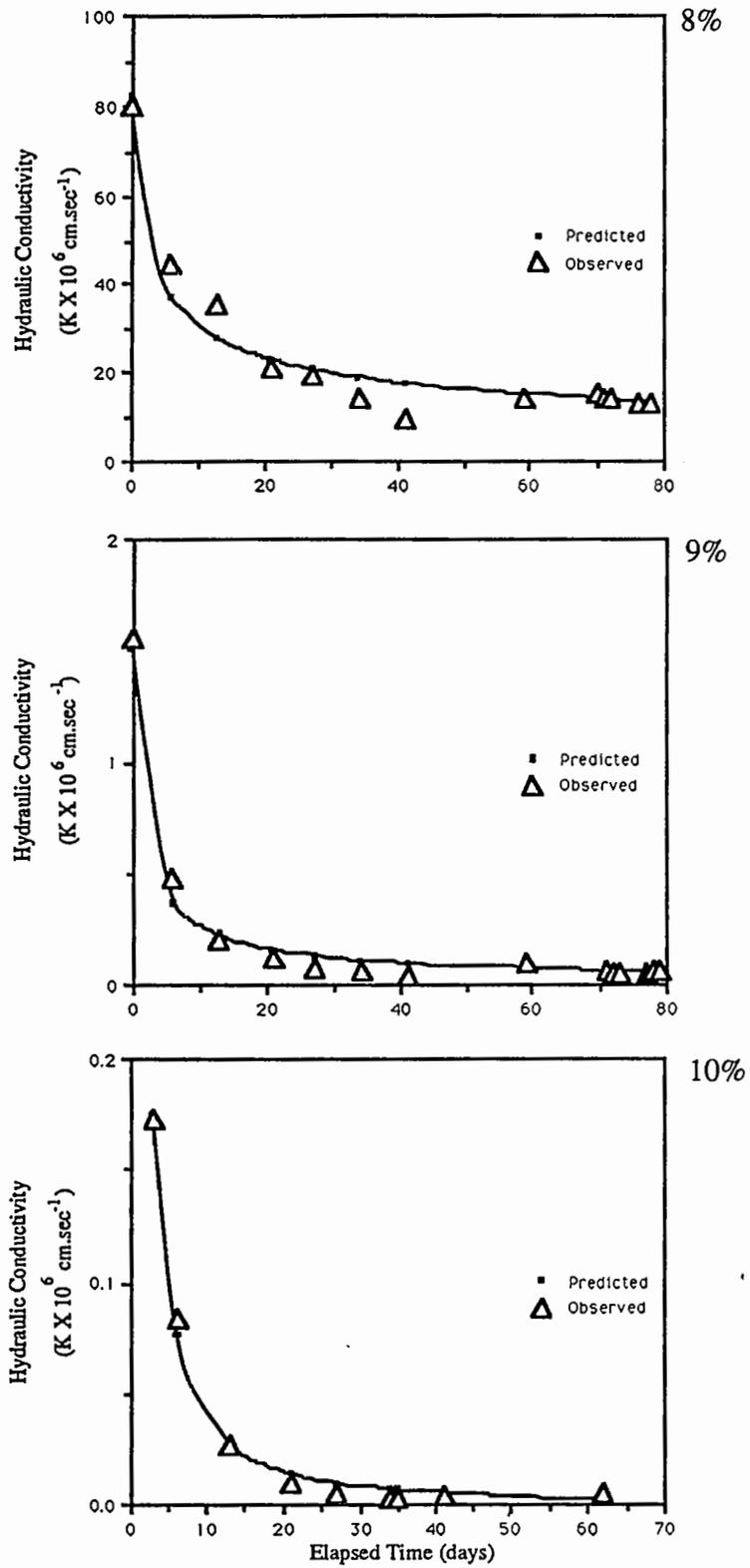


Figure 2. Variation of Hydraulic Conductivity with Time at 8%, 9% and 10% Matrix

The decrease in hydraulic conductivity was modelled according to the equation:

$$K \times 10^6 = A (T + 1)^B$$

where T is elapsed time measured from the first day of testing (T=0) and A and B are the intercept (initial condition) and slope of the power function, respectively. The regression results are summarized in Table 4, showing the statistical significance of the models.

**TABLE 4. MODEL COEFFICIENTS\* FOR THE CHANGE IN HYDRAULIC CONDUCTIVITY WITH TIME**

Matrix	Initial Value (A)	Standard Error	Slope (B)	Standard Error
8%	82.400	±4.361	-0.413	±0.025
9%	1.571	±0.044	-0.743	±0.032
10%	1.356	±0.148	-1.476	±0.070

\* regressions are significant at  $p < 0.001$ ; the models explain 98% (minimum) of the variation in hydraulic conductivity.

The models predict that with time hydraulic conductivity approaches "zero", but in fact this will never be achieved. However, if no future dissolution occurred, hydraulic conductivity for the system studied would not be the most important waste parameter affecting environmental loading. Leaching from sample surfaces and gross defects (cracks) would have the largest impact on waste transport, rather than transport from within the interior by permeant flow.

The phenomenon of reduced hydraulic conductivity with time has been observed with hardened cement pastes. Powers et al. (16) noted that the hydraulic conductivity of cement pastes cured underwater was reduced by six orders of magnitude due to increased hydration. Powers et al. (17) described the mechanism of this phenomenon whereby volume of hydrated paste is 2.1 times greater than unhydrated paste and hydration products fill pores and cavities, causing discontinuities, effectively reducing the number of flow channels. The number and radii of conducting capillary pores appear to define hydraulic conductivity in cement pastes. Nyame and Illston (18) compared their hydraulic conductivity data to that predicted by hydraulic radius theory and suggested a correlation. Hughes (19) considered the effects of pore characteristics (isotropy and tortuosity) in developing a model for cement-paste hydraulic conductivity which considered conducting channels as Poiseuille tubes.

The change in hydraulic conductivity with respect to time (slope), the "B" coefficient (Table 4), shows that hydraulic conductivity decreases more rapidly as the cement content increases. This indicates aqueous permeant-matrix interactions, specifically cement hydration during hydraulic conductivity testing. Cement hydration may be promoted by passing aqueous

permeant through the sample during hydraulic conductivity measurement. Samples of tested material were examined by scanning electron microscopy. Typical micrographs are shown in Figures 3a and 3b. Inlet portions show profuse "fibrous" growth in sample pores (Figure 3a). Sample portions covered by the latex membrane sidewall where permeant flow is restricted do not show this profuse fibrous growth. Patel et al. (20) noted a similar phenomenon that large pore fractions decreased while gel (paste) porosity increased during cement paste hydration.

X-ray analyses by STEM of individual fibres, dispersed on a carbon coated copper grid, yielded atomic ratios of Ca/S ranging from 1.75:1 to 2.67:1, as well as significant Al and traces of Fe. This suggests that the fibres are a calcium sulphoaluminate (AFt) phase of hydrated cement related to ettringite,  $3 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3 \text{ CaSO}_4 \cdot 31 \text{ H}_2\text{O}$ . The morphology of the observed fibres is similar to that of the AFt fibres described by Dalglish and Pratt (21).

The results of hydraulic conductivity and electron microscopy analyses show that cementitious wastes will react intimately with aqueous permeants and that cement hydration reactions continue for some time. This suggests that hydraulic conductivity regulations should consider temporal effects, by specifying sufficient replication over time, to measure permeant-matrix interactions. These interactions will likely vary between SS treatment techniques and should be studied on a case by case basis.

Caution is in order when predicting the long term behaviour of wastes based on short term tests. The hydration reactions discussed above are no doubt promoted by passing water through the samples during testing in an accelerated test. Not all hydration products may prove ultimately beneficial. Ettringite for example is formed during the sulphate attack of cements destroying its monolithic properties.

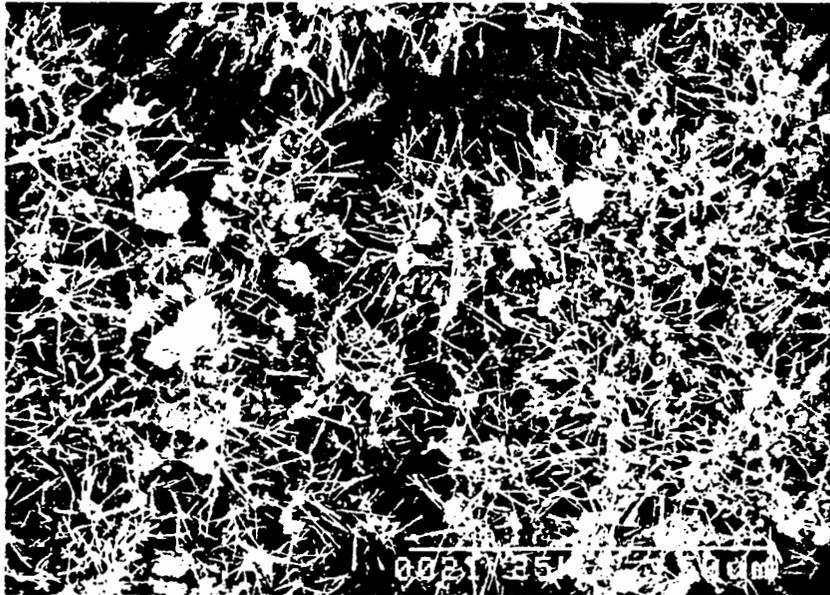
## RESPONSE SURFACE REGRESSION ANALYSES

Hydraulic conductivity data were collected for 8% and 9% matrix and showed that the overall mean hydraulic conductivity was significantly greater ( $p \leq 0.01$ ) for the 8% matrix ( $10 \pm 5 \times 10^{-6} \text{ cm} \cdot \text{sec}^{-1}$ ) compared to the 9% matrix ( $0.06 \pm 0.03 \times 10^{-6} \text{ cm} \cdot \text{sec}^{-1}$ ). For the waste system and measurement method, chosen hydraulic conductivity can differentiate between matrix treatments even when the confounding factors of time and instrument measurement parameters are retained.

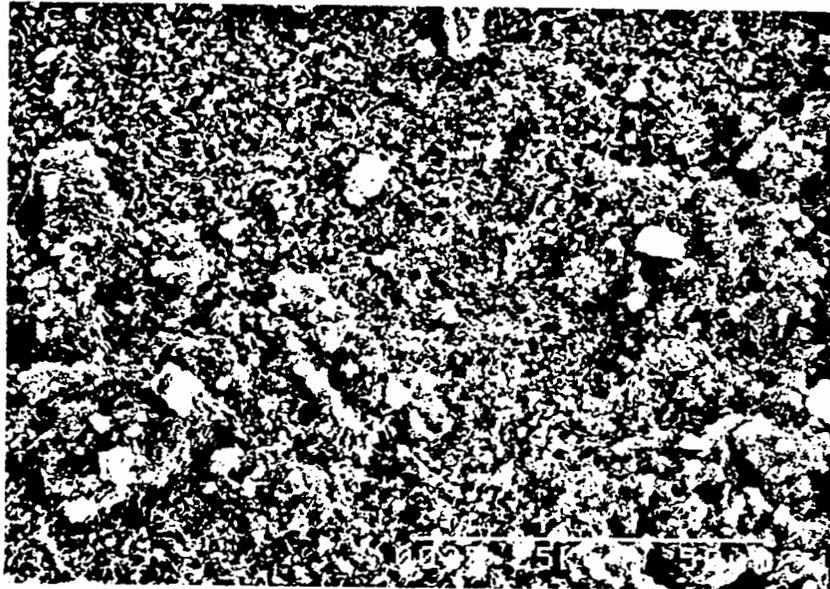
The variation in hydraulic conductivity with gradient and back pressure was modelled by a second order polynomial:

$$K \times 10^6 = b_0 + b_1x_1 + b_2x_2 + b_{11}x_1^2 + b_{22}x_2^2 + b_{12}x_1x_2$$

where  $x_1$  and  $x_2$  are the normalized (-1 to +1) gradient and back pressure, respectively.



a. Permeant Inlet Portion



b. Sidewall Portion

Figure 3. Scanning Electron Microscopy Photographs of SS Waste After Hydraulic Conductivity Testing

The results of the regression analysis are summarized in Table 5 using coded levels of the test parameters. The predicted hydraulic conductivity contours are shown in Figure 4 using decoded levels of the test parameters.

The linear effect of gradient was significant in both matrices but the effect of back pressure was significant at only 9% matrix. A negative quadratic component for gradient was noted for the 8% matrix.

The largest variation in hydraulic conductivity was less than five-fold as a result of increasing gradient and back pressure from low levels close to field conditions to the high levels used in accelerated testing. (This insensitivity to pressure factors suggests that the samples were highly liquid saturated.) Therefore laboratory measurements conducted to accelerate testing are a reasonable approximation of field conditions.

The hydraulic conductivity contour intervals suggest that hydraulic conductivity is less sensitive to changes in gradient and back pressure at medium and high levels. Regulatory tests could minimize variance by specifying relatively high levels of gradient ( $i = 227, 343$  kPa across a 15 cm sample) and back pressure (124 kPa) for testing hydraulic conductivity.

## CONCLUSIONS AND RECOMMENDATIONS

For the SS waste analyzed in this study:

- 1) Hydraulic conductivity was very sensitive to matrix, a difference of only one percent in cement and water content yielded statistically different results.
- 2) Sample bulk density was a practical and useful quality assurance parameter to minimize variability in hydraulic conductivity measurements. By applying an acceptance criterion of  $\pm 0.5\%$  from the mean, a difference of three orders of magnitude in hydraulic conductivity was observed between samples differing only by 1% in nominal cement content.
- 3) A permeant-matrix interaction occurred, which reduced hydraulic conductivity as the test progressed. A plausible explanation, based on electron microscopy and dispersive x-ray analysis, is the formation of hydration products which 'plug' the conducting pores in the matrix.
- 4) The temporal effects resulting from the above interaction can be described by mathematical models, which suggest that in the absence of other effects, such as matrix dissolution, the impact of hydraulic conductivity on contaminant leaching will be reduced with time.

**TABLE 5. RESPONSE SURFACE REGRESSION ANALYSES**

Matrix (wt%)	$b_0$	$b_1$	$b_2$	$b_{11}$	$b_{22}$	$b_{12}$	n	$r^{2†}$	LOF <sup>‡</sup>	p <sup>*</sup>
8 (s.e.)	13.01** (0.826)	2.33** (0.691)	0.18 (0.728)	-4.30** (1.106)	-1.21 (1.101)	-0.32 (0.846)	22	0.68	n.s. <sup>#</sup>	0.001
9 (s.e.)	0.06** (0.005)	0.02** (0.005)	0.01** (0.005)	-0.01 (0.008)	0.003 (0.0077)	-0.001 (0.0063)	26	0.58	n.s.	0.002

† $r^2$  = coefficient of determination (variance described by the model)

‡LOF = (Lack of Fit Test)

\*p = probability of a Type I error

\*\* = Significant Effect ( $P \leq 0.01$ )

#n.s. = not significant at  $P \leq 0.05$

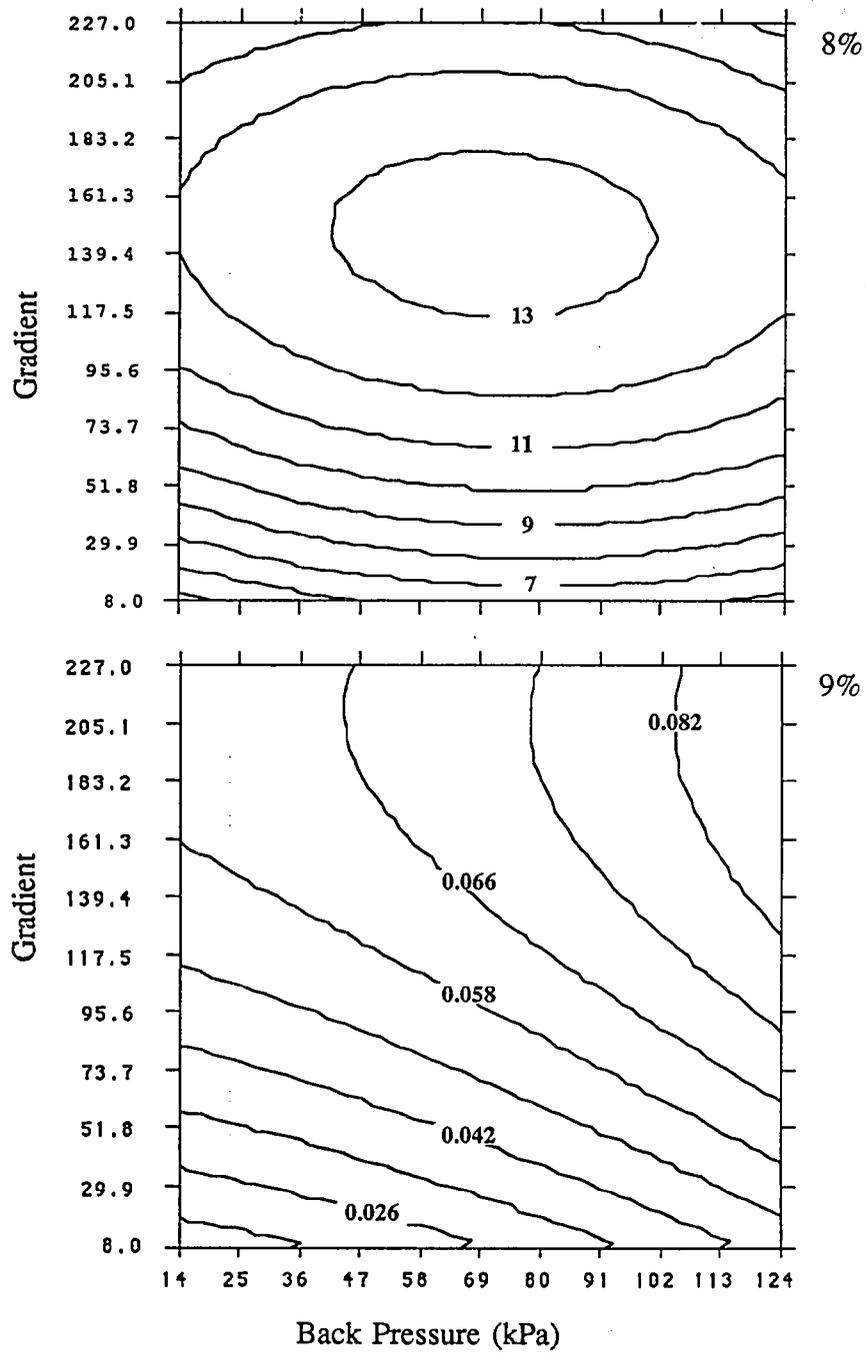


Figure 4. Contour Plots from Response Surface Analysis for 8% and 9% Matrix

- 5) The effects of gradient and, for the 9% matrix, back pressure were statistically significant, and the sensitivity of hydraulic conductivity was less at higher levels of these parameters.

General recommendations for regulatory test development:

- 1) Bulk density should be used as a quality assurance parameter to minimize sample preparation variability.
- 2) To estimate maximum field hydraulic conductivity, measurement should be made as soon as the sample is cured.
- 3) To minimize variability, temporal effects should be taken into account and measurements carried out at high levels of gradient and back pressure when 'equilibrium' is reached.

### ACKNOWLEDGEMENTS

We gratefully acknowledge the assistance of Dr. Doug Ivey, Dr. Randy Mikula and Dr. Maria Neuwirth in providing SEM, STEM and x-ray analyses, Mr. Philip Henry in providing graphics, and Ms. Connie Jackson and Ms. Patricia Soldan in preparing the manuscript.

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OZONE-ULTRAVIOLET LIGHT TREATMENT OF IRON CYANIDE COMPLEXES

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ABSTRACT

Recent concern over the quantity of total cyanide being disposed of in landfills and discharged to surface water has prompted the US Environmental Protection Agency Office of Solid Waste to begin investigating alternative treatment technologies for the destruction of total cyanide present in electroplating wastewaters. Combined ozonation and ultraviolet light irradiation was evaluated at the US EPA Test & Evaluation Facility for the destruction of ferricyanide complex, a stable metal cyanide complex that is not destroyed by conventional treatment technologies. Effects of temperature, UV light intensity, and reactor configuration on the destruction rate were studied in this work.

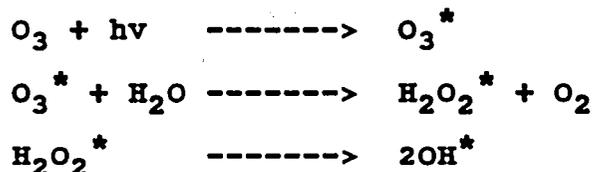
Results from this study confirm that an initial ferricyanide concentration of 150 mg/L can be reduced to less than 1 mg/L in 4 hours using an UV intensity of 3 W/L, temperature of 63.2°C and an ozone dose of 56.5 mg/min/L in a reactor where the ozone bubbles are dispersed right below the UV lamps submerged in the solution. Ozone saturation concentrations and mass transfer coefficients for ozone were found to decrease with temperature and UV light intensity. At 22.2°C the ozone saturation concentration was 10.7 mg/L and the mass transfer coefficient was 0.3 min<sup>-1</sup>. In a simultaneous study it was found that irradiating ozone in an external chamber (gas phase) with subsequent introduction of the irradiated ozone into the liquid phase produces very little destruction of the ferricyanide complex.

## BACKGROUND

Ferricyanide,  $[\text{Fe}(\text{CN})_6]^{3-}$ , is the most abundant metal cyanide complex remaining in the electroplating and metal finishing waste streams following alkaline chlorination or ozonation (1). Other iron cyanide complexes such as ferrocyanide are quickly oxidized to the stable ferricyanide during such treatment (2). The resistance of ferricyanide to conventional treatment is not completely understood, but previous work has shown it can be destabilized and oxidized in the presence of ozone and ultraviolet light (1,3,4,5,6).

A review of the literature on the decomposition of ferricyanide by simultaneous UV irradiation and ozonation ( $\text{O}_3/\text{UV}$ ) uncovered some inconsistencies between the conclusions of previous researchers. There is also a shortage of data required for further process design. Prober and Melnyk (6), have shown that reaction rates for the oxidation of ferricyanide by  $\text{O}_3/\text{UV}$  are dependent on UV intensity and not temperature, whereas Prengle and Mauk (5) have shown that temperature has a significant effect on the rate of ferricyanide decomposition by  $\text{O}_3/\text{UV}$  (three-fold increase in the reaction rate when the temperature is raised from 25°C to 66.5°C). Prober and Melnyk, however, show an insignificant change in the reaction rate when the temperature is raised from 25°C to 50°C.

Another discrepancy found in the literature was the actual function of UV light. Garrison and Mauk (1) believed that ferricyanide was destabilized by UV light, making it more susceptible to ozone oxidation. On the other hand, research by Prober and Melnyk, using various reactor configurations have shown significant decreases in reaction rates when ozone is shielded from UV light within the same reactor. These results suggest that the primary function of UV light is to activate the ozone (forming hydroxyl radicals) which then oxidizes the ferricyanide complex. The following mechanism has been suggested by Ashmore (7), Barker (8), Peyton (9), and Wallace (10), for the activation of ozone by UV light:



The relative reactivity of hydroxyl radicals is illustrated in Table 1 where reaction rates with classes of organic compounds are compared to those of ozone (8). As shown, reaction rates increase by orders of magnitude for hydroxyl radicals as

compared to ozone.

It has been postulated that activation of ozone by UV light (excitation of electrons from the 3-P orbital to the 1-D orbital of the oxygen atoms) takes place in the gaseous phase, with hydroxyl radical formation occurring at the bubble interface. If this postulation is correct, then ozone can be activated by UV light outside the reacting solution, with hydroxyl radical formation occurring once the activated ozone contacts water. Also, if activation of ozone can be achieved in the gaseous phase then typical problems such as hindrance by wastewater turbidity can be eliminated. In addition, since air has less resistance to penetration by UV light than water, less electrical power would be required to achieve the same hydroxyl radical formation. It is, therefore, necessary to study the effects of ozone activation, in the gaseous phase, on the destruction of ferricyanide.

In addition to the above process parameters, the mass transfer rate of ozone into the aqueous solution is also a critical parameter, since often the low mass transfer rate is the primary obstacle to the propagation of the reaction. Therefore, it is necessary to develop a reactor which will provide a high mass transfer rate of ozone.

#### OBJECTIVES

The objectives of the study were as follows:

- A. Develop a reactor which will provide a high mass transfer rate of ozone and intimate contact of ozone bubbles and UV light. Determine the saturation concentrations of ozone in water and the mass transfer rates at two different temperatures and two different UV light intensities.
- B. Determine the rate at which  $O_3/UV$  can oxidize an iron cyanide solution containing 150 mg/L of cyanide.
  1. Determine the effects of UV light intensity on the reaction rate for the oxidation of ferricyanide.
  2. Determine the effects of temperature on the reaction rate for the oxidation of ferricyanide.
- C. Determine the effects of ozone activation by UV light in the gas phase prior to contacting the liquid phase.

#### EXPERIMENTAL SETUP

The complete study was performed in a semi-batch mode in the laboratory using a 2-liter stainless steel reaction

vessel. Figure 1 presents a diagram of the reaction system including the ozone generator, the stainless steel reactor and the gas washing bottles. Figure 2 is a cross sectional diagram of the reactor showing the UV lamps, thermometer, and ozone sparser. The mixer was a centrifugal pump from which the plastic stationary housing containing the suction and discharge ends had been removed in order to expose the impeller. The pump was mounted vertically through an orifice in the reactor base plate such that the impeller was located on the floor of the reactor. Various degrees of mixing were achieved by changing the power input to the mixer motor using a voltage controller.

Samples from the reactor were obtained through a rubber septum fitted into a Swagelock fitting in the reactor lid. Syringes, varying in sizes from 1 ml to 10 mls, and fitted with 6-inch piercing needles were used to draw samples from the mid-section of the reactor. Both filling and emptying of the reactor was accomplished by removing the sample port Swagelock fitting and inserting a funnel or 1/2 inch plastic siphon hose, depending upon the operation.

Heating tape was wrapped around the entire length of the reactor to supply heat to the reactor for the high temperature operations. The tape was insulated to reduce heat loss. The power to the heating tape was controlled through a voltage controller. When necessary ice packs were used to maintain the reactor at 22.2°C.

The ozone generation system was a PCI Model G-2 ozone generator rated at a maximum output of 2.0 lbs/day at 2% concentration in combination with a PCI Model ADP-1 air preparation unit. The ozone generator was fed prepurified lab air at ambient temperature. Two liters of the ozonated air was delivered into the reactor and the excess was vented into the exhaust system. Using absorption in potassium iodide solution and subsequent titration, the ozone delivery rate to the reactor was determined to be  $113 \pm 11.3$  mg/min. Ozone which entered the reactor traveled down a glass tube to a fritted bubble stone positioned 3/4 inches above the mixing impeller. Exhaust gases from the reactor could be passed through potassium iodide traps to determine the quantity of the unused ozone.

The UV lamps, selected for this study, were submersible, short wave (254 nm), low pressure mercury ultraviolet lamps with a maximum power rating of approximately 3 watts per lamp. Each UV lamp was powered by a separate power supply. UV light intensity in the reactor could be varied by changing the number of UV lamps used during the reaction. The lamps were positioned in such a way that ozone bubbles, coming out of the

sparger at the reactor bottom, traveled along the length of the UV lamps.

All of the experiments were performed at the U.S. EPA Test and Evaluation Facility located in Cincinnati, Ohio.

## PROCEDURES, RESULTS AND CONCLUSIONS

### A. OZONE SATURATION CONCENTRATIONS AND MASS TRANSFER COEFFICIENTS

#### Procedure

To determine the transfer of ozone to the stainless steel reactor, two liters of distilled water were added and the reactor purged for 15 minutes with prepurified air to remove any residual volatile organics. The temperature of the water and reactor were adjusted to the predetermined set point (22.2°C or 63.2°C) using heating tapes or ice packs. The mixing rate was adjusted to 1600 rpm using the variable voltage controller. The ozone charged air leaving the ozone generator was fed to the bottom of the reactor, where it was dispersed into the liquid phase through a fritted bubble stone. One set of test runs was performed without any UV lamps and the other set was performed with an UV intensity of approximately 3 W/L. For each set of conditions the absorption runs were made in triplicate.

Samples of the ozonated solution were collected at 1 minute intervals for the first 5 minutes of the ozone absorption study and at 5 minute intervals for the remaining 60 minutes of the run. The samples were immediately spiked into 20 mls of 2% w/w potassium iodide solution to trap the dissolved ozone. This solution was then titrated with sodium thiosulfate and the ozone concentration in the distilled water was determined.

#### Results

Figure 3 presents a plot for the typical average ozone concentration vs. time data for one of the four above mentioned absorption runs. Ozone saturation concentrations in the distilled water were determined from the concentration vs. time plots. The ozone saturation concentration for three of the above mentioned four sets of conditions were 10.7 mg/L (at 22.2°C), 7.9 mg/L (at 63.2°C) and 5.4 mg/L (at 22.2°C with 3 W/L UV intensity). At 63.2°C with 3 W/L UV intensity the ozone concentration in the water was below the detection limit (1.5 mg/L) for the entire period of the absorption run.

From the ozone saturation concentrations and the absorption data, the mass transfer coefficients ( $K_L a$ ) for ozone were determined. By relating the first few minutes of absorption data for the various conditions (UV intensity and temperature) and the maximum solubility of ozone for that condition, the data required to determine the coefficient were calculated. The  $K_L a$  values for the above mentioned conditions were  $0.30 \text{ min}^{-1}$  (at  $22.2^\circ\text{C}$ ),  $0.22 \text{ min}^{-1}$  (at  $63.2^\circ\text{C}$ ), and  $0.18 \text{ min}^{-1}$  (at  $22.2^\circ\text{C}$  with 3 W/L UV intensity).

### Conclusions

The absorption data obtained for ozone in the bench-scale reactor correlated well with the values obtained by previous researchers. Ouederni (11), using a semi-batch reactor, obtained an ozone saturation concentration of approximately 12.5 mg/L at  $20^\circ\text{C}$ . Also, from the data it was concluded that saturation concentration of ozone decreases with increase in temperature or UV light intensity. This is most likely due to the faster rate of ozone decomposition at higher temperature and higher UV light intensity.

The mass transfer coefficient of  $0.3 \text{ min}^{-1}$  at  $22.2^\circ\text{C}$  is significantly higher than the values obtained by other researchers (12) which are presented in Table 2. Assuming that there were no errors in the measurements and calculations it was concluded that the fabricated reactor provided a high mass transfer rate of ozone. The results also show that the mass transfer coefficient decreases with increase in temperature and UV light intensity.

### B. EFFECTS OF TEMPERATURE AND UV LIGHT INTENSITY ON THE DESTRUCTION OF FERRICYANIDE

#### Procedure

In order to determine the effects of increased temperature and UV light intensity a systematic testing program involving both parameters was devised. Table 3 presents the various UV light intensities and temperatures tested.

The initial total cyanide concentration for this portion of the study was 150 mg/L. Examination of the various reaction rates published in the literature for the oxidation of ferricyanide showed the probable rate constant ( $K$ ) to be  $0.017 \text{ min}^{-1}$ . Assuming the reaction to be first order and the reaction system to act as a completely stirred tank reactor (CSTR) it was calculated that a reaction time of 230 minutes is required for a 98 percent removal of total cyanide. The actual run time was extended to 240 minutes to ensure a complete 98 percent removal.

Treatment of ferricyanide in the bench-scale reactor began by starting the reactor mixer and adjusting the temperature to either 22.2°C or 63.2°C, depending upon the specific run conditions. Once the proper temperature was attained, the required number of UV lamps were turned on and the ozone flow to the reactor was initiated. Ozone off-gas was passed through the potassium iodide solutions to determine the quantity of ozone exiting with the off gas. Samples were collected from the reactor at various times throughout the treatment run as shown in Table 4. Samples were immediately diluted to 1 liter in a volumetric flask with 0.01 N sodium hydroxide solution (pH>11) to halt any further reaction (13) and to provide the required volume for analysis.

### Results

Table 5 summarizes the total cyanide concentrations in the reactor following the 4-hour test period for each set of conditions. These concentrations are averages of three runs conducted for each set of conditions. Cyanide concentration histories for all of the different sets of conditions are plotted in Figure 4.

### Conclusions

From the final cyanide concentration data, for runs under different sets of conditions, it was concluded that changing the temperature from 22.2°C to 63.2°C resulted in a significant increase in the reaction rate while changing the UV light intensity from 1.5 W/L to 3 W/L produced only a moderate increase in the reaction rate. Neither UV light nor ozone, used by itself, produced any significant destruction of the ferricyanide complexes.

The results of this study confirmed that ozone/UV oxidation is a potentially effective treatment technology for iron cyanide complexes. Ferricyanide concentrations of 150 mg/L (as cyanide) can be reduced to less than 1 mg/L in 4 hours of treatment at a temperature of 63.2±0.5°C, an ozone dose of 56.5 mg/min/L, and UV light intensity of 3 W/L.

From the results of this study and some other previous investigations it is concluded that destruction of ferricyanide will occur only if ozone bubbles are exposed to UV irradiation in the reactor. Irradiating the ferricyanide solution only prior to ozonation or ozonated ferricyanide solution does not achieve any significant destruction of the iron cyanide complexes.

## C. EFFECTS OF OZONE ACTIVATION BY UV LIGHT IN THE GAS PHASE

### Procedure

For this study, the bench-scale reactor was modified such that a single UV lamp was suspended above the reactor in an air tight glass chamber. Ozone was passed from the top of the chamber, along the light and out the bottom, where it was routed into the reactor. All gas flow rates, ozone delivery rates and reactor mixing rates were identical to those performed earlier. Since only one light was used in this study, UV intensity was 1.5 W/L. A temperature of 63.2°C was used for this run.

### Results

The results of this run showed that little or no destruction of cyanide was achieved.

### Conclusions

The test failed to confirm the hypothesis that ozone activation by UV irradiation in the gaseous phase can provide similar results as ozone activation in the solution. One possible reason is the delay between exposure of ozone to UV light in the external chamber and its entrance into the reactor where it is supposed to form the hydroxyl radicals. According to Ashmore (7) the time of excitation and subsequent loss of radical activity is in the order of microseconds whereas the lapsed time in this system was approximately 0.5 seconds.

## RECOMMENDATIONS

Since it is important to irradiate the ozone bubbles by the UV lamps, the reactor design should ensure such irradiation. In a large reactor UV lamps with ozone spargers right below the lamps should be distributed in a grid system along the cross section of the reactor. Distances between the UV lamps should be inversely proportional to the amount of solids formed during the reaction. Another way of reducing the number of UV lamps with ozone spargers is to incorporate solids removal devices in between stages of a multistage reactor.

Since ozone transfer to the liquid is never complete it is desirable to utilize the ozone in the exhaust gas rather than to destroy it or release it into the atmosphere. One possible way of utilizing the ozone in the exhaust gas would be to use a dual-stage reactor with fresh ozone entering the second stage, where the highly stable metal-cyanide complexes will be destroyed, and exhaust gas from the second stage going into the

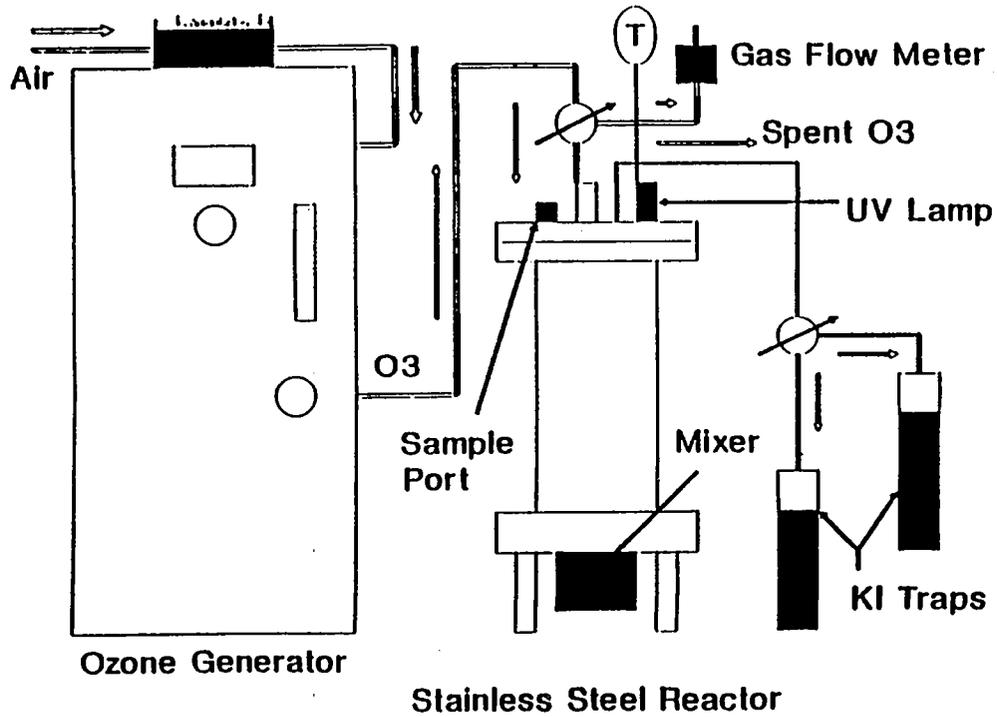
first stage where free cyanides and some less stable metal-cyanide complexes will be destroyed. This setup would be highly applicable to the electroplating industry wastes which contain both free and complexed cyanides.

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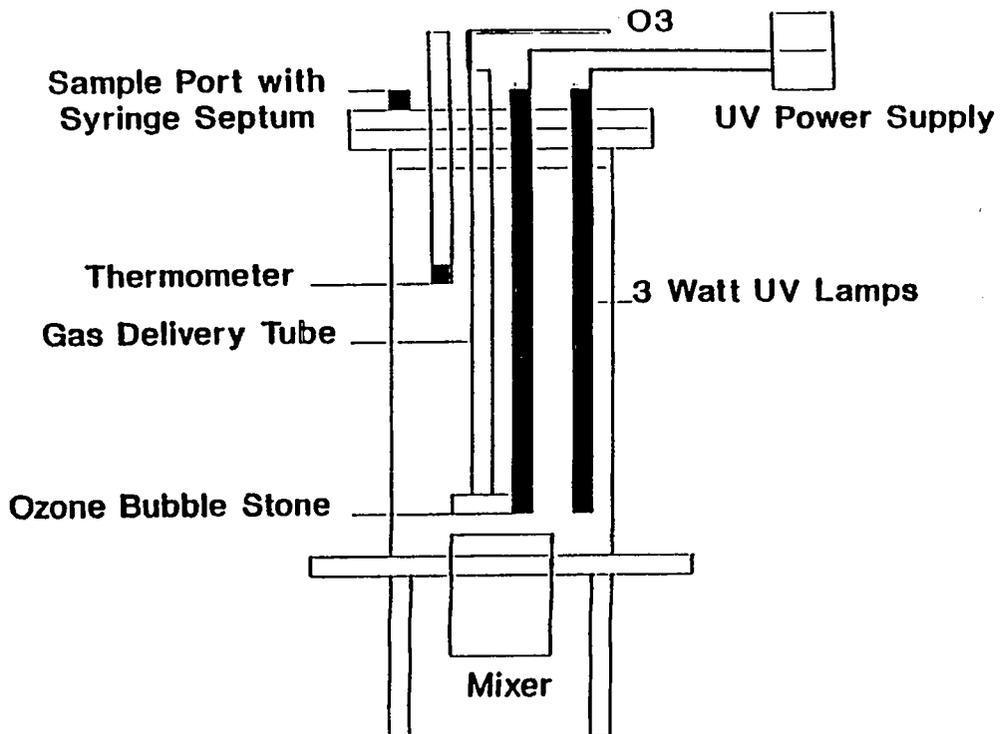
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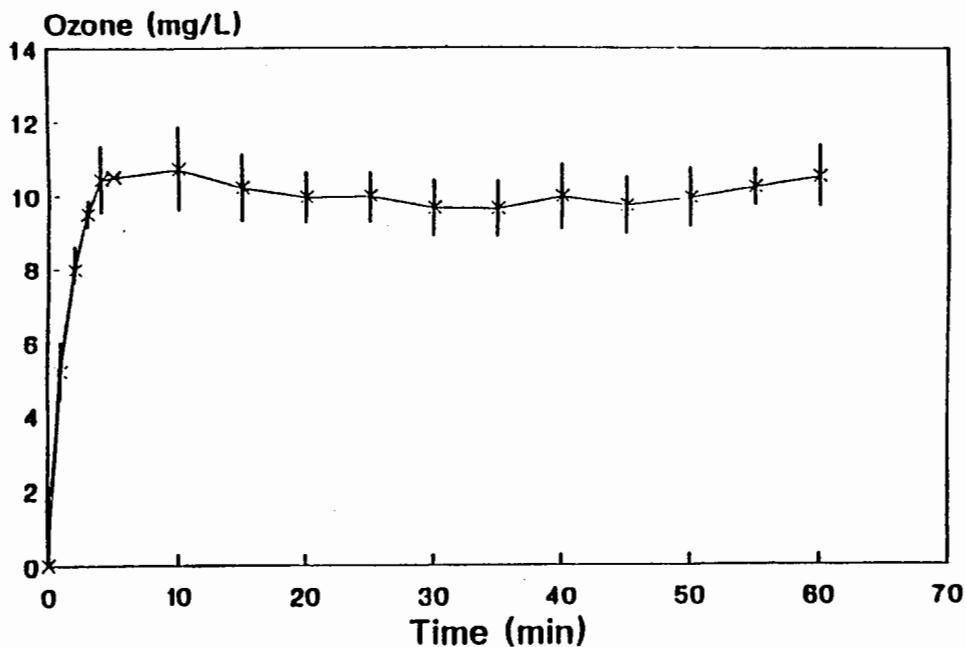
**FIGURE 1 OZONE/UV TREATMENT SYSTEM**



**FIGURE 2 Cross Section of Reactor**

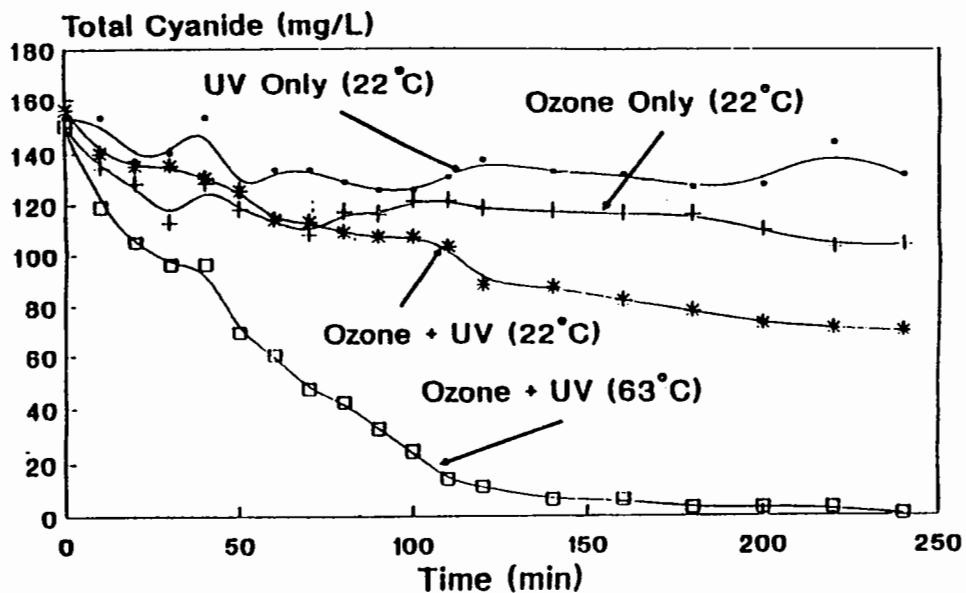


**FIGURE 3**  
**Average Ozone Absorption in Water**



Temperature:  $22.2 \pm 0.9$  °C

**FIGURE 4**  
**Effect of Temperature and UV Intensity on the Removal of Ferricyanide**



All UV Intensities at 3 W/L

TABLE 1

COMPARISON OF REACTION RATES OF OZONE AND HYDROXYL RADICALS  
WITH CLASSES OF ORGANIC COMPOUNDS (8)

Compound	k (L/mole/s)	
	O <sub>3</sub>	OH
Olefins	1 to 450 x 10 <sup>3</sup>	10 <sup>9</sup> to 10 <sup>11</sup>
S-containing organics	10 to 1.6 x 10 <sup>3</sup>	10 <sup>9</sup> to 10 <sup>11</sup>
Phenols	10 <sup>3</sup>	10 <sup>9</sup>
N-containing organics	10 to 10 <sup>2</sup>	10 <sup>8</sup> to 10 <sup>10</sup>
Aromatics	1 to 10 <sup>2</sup>	10 <sup>8</sup> to 10 <sup>10</sup>
Acetylenes	50	10 <sup>8</sup> to 10 <sup>9</sup>
Aldehydes	10	10 <sup>9</sup>
Ketones	1	10 <sup>9</sup> to 10 <sup>10</sup>
Alcohols	10 <sup>-2</sup> to 1	10 <sup>8</sup> to 10 <sup>9</sup>
Alkanes	10 <sup>-2</sup>	10 <sup>6</sup> to 10 <sup>9</sup>
Carboxylic acids	10 <sup>-3</sup> to 10 <sup>-2</sup>	10 <sup>7</sup> to 10 <sup>9</sup>

TABLE 2

MASS TRANSFER COEFFICIENTS FOR OZONE INTO WATER DETERMINED BY  
VARIOUS RESEARCHERS (12)

Researcher	K <sub>L</sub> a (min <sup>-1</sup> )
Praserthdam	0.067 - 0.165
Tsuno	0.028 - 0.039
Jackson	0.044 - 0.048
Deckwer	0.028 - 0.144

TABLE 3

RUN CONDITIONS FOR TEMPERATURE AND ULTRAVIOLET LIGHT  
INTENSITY OPTIMIZATION

Run	Temperature (°C)	UV Intensity (W/L)	Ozone Dose (mg/min/L)	Number of Samples
A	21.1	0	56.5 ± 6	54
B	21.1	3.0	0	54
C	21.1	3.0	56.5 ± 6	54
D	21.1	1.5	56.5 ± 6	54
E	65.5	1.5	56.5 ± 6	54
F	65.5	3.0	56.5 ± 6	54

TABLE 4

SAMPLING FREQUENCY AND SAMPLE VOLUMES FOR TEMPERATURE AND  
ULTRAVIOLET LIGHT OPTIMIZATION RUNS

Portion of Run (min)	Sampling Interval (min)	Sample Volume (ml)
0-60	10	1
60-120	10	2
120-180	20	4
180-240	20	6

TABLE 5

TOTAL CYANIDE CONCENTRATIONS AFTER 4 HOURS OF TREATMENT

Ozone (mg/min)	UV Light (W/L)	Temperature (°C)	Total Cyanide (mg/L)
0	3	22	131
113	0	22	104
113	1.5	22	91
113	3	22	71
113	1.5	63	10
113	3	63	0.6

DEVELOPMENT OF LDR STANDARDS  
FOR CONTAMINATED SOIL AND DEBRIS

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ABSTRACT

The RCRA Land Disposal Restrictions (LDRs) require that soil and debris that are contaminated with hazardous waste be treated prior to land disposal. Soil and debris from Superfund remedial actions, RCRA corrective actions, and possibly underground storage tank (UST) sites that are destined for land disposal will be affected by the LDR regulation. Recognizing that Superfund soil and debris would be much more difficult to treat than many of the industrial process wastes that were used to develop the existing LDR best demonstrated available technology (BDAT) standards, the EPA Office of Emergency and Remedial Response (OERR) launched an effort to investigate the treatability of soil. Existing soil treatment data were collected in 1987 and 1988. The data collected were used in the development of alternate treatability variance levels for soil and debris and were summarized in the "Summary of Treatment Technology Effectiveness for Contaminated Soil" (1). EPA is actively involved in the collection of additional data on the treatment of soil and debris which will be used in the development of the LDR regulations for soil and debris. The purpose of this paper is to summarize what OERR has learned about soil treatment effectiveness and to present the technical issues that EPA is facing in the development of the final treatment standards.

INTRODUCTION

Section 3004(m) of the Resource Conservation and Recovery Act (RCRA) mandates that the EPA require treatment of hazardous wastes prior to land disposal. Known as the "Land Disposal Restrictions" (LDRs), these regulations may apply to hazardous industrial process wastes as well as contaminated soil, sludge

and debris from Superfund and RCRA facilities that are destined for land disposal.

The 1989 Superfund Management Review (also known as the 90-Day Study) by the Office of Solid Waste and Emergency Response (OSWER) acknowledged that Superfund response actions may not be able to meet existing RCRA treatment standards based on "best demonstrated available technology" (BDAT) under the LDRs. The existing LDR regulations may limit the potential treatment technologies available for Superfund clean-ups, with technologies such as soil washing, stabilization, and biological treatment, being precluded because they may not meet the highest level of performance required by LDRs. In contrast, the 90-Day Study encouraged the greater use of innovative technologies and urged the reduction of non-technical barriers, such as regulatory and policy constraints, that inhibit the use of treatment technologies, while preserving the intent and spirit of applicable RCRA regulations.

OSWER recognized the potential limitation on treatment technologies for Superfund actions and developed a process to use LDR treatability variances for soil and debris. Guidance was issued to the Regions through the Superfund LDR Guide 6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions," (OSWER Directive 9347.3-06FS) in July 1989 and revised in September 1990 (2). Superfund LDR Guide 6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions," (OSWER Directive 9347.3-07FS) was issued in December 1989 and revised in September 1990 (3). These guides describe the treatability variance process, include alternate treatment levels to be obtained under treatability variances, and identify treatment technologies which have achieved the recommended levels.

A memorandum issued on November 30, 1989 by OSWER entitled the "Analysis of Treatability Data for Soil and Debris: Evaluation of Land Ban Impact on Use of Superfund Treatment Technologies," (OSWER Directive 9380.3-04) provides support for decisions by the Regions to use treatability variances, when appropriate (4). The analysis identifies some of the key technical considerations to be evaluated in obtaining a treatability variance.

OSWER recognizes that the use of treatability variances represents an interim approach and is actively in the process of acquiring additional data for developing separate treatment standards for contaminated soil and debris.

The collection of data which supports the development of regulations for contaminated soil and debris is a joint effort by the OSWER's Office of Emergency and Remedial Response (OERR), Office of Solid Waste (OSW), and Technology Innovation Office

(TIO), and the Office of Research and Development (ORD) Risk Reduction Engineering Laboratory (RREL). The initial data collection effort by the OERR that produced the data for the development of the treatability variance levels also identified the types of data needed to develop treatment standards for soil. This paper describes both the conclusions drawn by OERR to date as well as the unique considerations of soil treatment which require further investigation. Ongoing data collection and evaluation activities are also described.

#### ANALYSIS OF TREATMENT EFFECTIVENESS

OERR launched an extensive effort in 1987 and 1988 to collect existing data on the treatment of soil, sludge, debris, and related environmental media. The results from several hundred studies were collected and reviewed.

All applicable treatment information from the best documented studies was extracted, loaded into a data base, and analyzed to determine the effectiveness of technologies to treat different chemical groups (1).

Based on this analysis, a number of technologies commonly used in the Superfund program provide substantial reduction in mobility and toxicity of wastes as required in Section 121 of the Superfund Amendments and Reauthorization Act (SARA) of 1986. For example:

- o Thermal destruction has been effective on all organic compounds, usually accomplishing well over 99% reduction of organics.
- o Although the data indicate that PCBs, dioxins, furans, and other aromatic compounds have been dechlorinated to approximately 80%, more recent data indicate that removal efficiencies may approach 99.9%.
- o Bioremediation successfully treats many halogenated aliphatic compounds, non-halogenated aromatics, heterocyclics, and other polar compounds with removal efficiencies in excess of 99%.
- o Removal efficiencies for low temperature thermal desorption have been demonstrated with averages up to 99% for non-polar halogenated aromatics and with treatment often exceeding 90% for other polar organics.
- o Soil washing and chemical extraction data on organic compounds indicate average removal efficiencies of approximately 90% for polar non-halogenated organics and 99% for halogenated aromatics, with treatment often

exceeding 90% for polynuclear aromatics. The soil washing process, with optimized solvent selection, has demonstrated removal efficiencies often exceeding 90% for volatile and non-volatile metals.

- o Immobilization can achieve average reductions in mobility of 93% for volatile metals, with reductions in mobility often exceeding 90% for non-volatile metals. Immobilization processes, while not actually destroying the organic compounds, reduce the mobility of contaminants an average of 99% for polynuclear aromatic compounds. Immobilization may not effectively stabilize some organic compounds, such as volatile organics, and the long-term effectiveness of immobilization of organics is under evaluation.

#### CONCLUSIONS REGARDING SOIL TREATMENT TECHNOLOGY EFFECTIVENESS

Contaminated soils can be treated via three basic mechanisms: (1) destruction of the contaminants through alteration to a less toxic compound; e.g., thermal destruction, dechlorination, bioremediation; (2) physical transfer and concentration of the contaminants to another waste stream for subsequent treatment or recovery; e.g., low temperature thermal desorption and chemical extraction, soil washing; and (3) permanent bonding of the contaminants within a stabilized matrix to prevent future leaching; e.g., immobilization and vitrification. In general, the destruction technologies are effective in reducing the toxicity of many organic contaminants. The physical transfer technologies reduce the toxicity and often the volume of selected organic and inorganic contaminants. While the bonding technologies are most effective at reducing the mobility and, therefore, the toxicity of inorganic contaminants, some increasing effectiveness is being demonstrated on selected organic contaminants as well. Figure 1 presents a summary of these basic conceptual conclusions. A more detailed discussion follows.

The technologies that have been widely demonstrated on soils are thermal destruction for organic contaminants and immobilization for inorganic contaminants. While these two technologies may be highly effective in treating particular classes of compounds, neither provides an ideal solution to complex mixtures of organic and inorganic contaminants, which are common at Superfund sites. The inherent difficulty in treating contaminants in a soil matrix, where waste conveyance and mixing are in themselves complicated unit operations, contributes to the need to find special solutions. Other issues, such as landfill capacity and cost, cross-media impacts, and natural resource conservation, also support the need to develop and use

Contaminant	Technology		
	Destruction	Physical Transfer	Stabilization
Volatile Organics	●	●	✘
Semi-Volatile Organics	●	◐	◐
Metals	✘	◐	●

- Demonstrated Effectiveness    ✘ Not Effective, Not Advised
- ◐ Potential Effectiveness  
(More Data Required)

**Figure 1. Soil Treatment Effectiveness - Conceptual Approach**

alternative and innovative treatment technologies for contaminated soil.

Because of EPA's ultimate goal of developing LDRs for contaminated soil and debris, this study evaluates a number of treatment options that are applicable to excavated soils. In-situ soil techniques, such as some types of bioremediation, soil vapor extraction, in-situ immobilization, and combined ground water and vadose zone soil treatment were not included in the scope of this evaluation. In-situ techniques should also be considered when researching remediation measures for a contaminated soil problem. When in-situ technologies are used at Superfund sites, the LDRs may not be applicable because the waste has not been excavated and subsequently "placed" in a landfill or other RCRA unit.

Based upon the data collected and evaluated by OERR from more than 200 soil treatment tests, conclusions were developed regarding the effectiveness of six soil treatment technology groups for each of eleven contaminant treatability groups. For destruction and physical transfer technologies applied to organic contaminants, the removal efficiency was analyzed. This evaluation factor was replaced by the reduction in mobility for the following technologies: immobilization, chemical extraction, and soil washing. The principles of operation and the effectiveness of treatment on organic and inorganic contaminants are presented below.

#### THERMAL DESTRUCTION

##### Principle of Operation

- o Thermal destruction uses high temperatures to incinerate and destroy hazardous wastes, usually by converting the contaminants to carbon dioxide, water, and other combustion products in the presence of oxygen.

##### Effectiveness on Organics

- o This technology has been proven effective on all organic compounds, usually accomplishing well over 99% removal.
- o Thermal destruction technologies are equally effective on halogenated, non-halogenated, nitrated, aliphatic, aromatic, and polynuclear compounds.
- o Incineration of nitrated compounds such as trinitrotoluene (TNT) may generate large quantities of nitrous oxides.

### Effectiveness on Inorganics

- o Thermal destruction is not an effective technology for treating soils contaminated with high concentrations of some metals.
- o High concentrations of volatile metal compounds (lead) present a significant emissions problem, which cannot be effectively contained by conventional scrubbers or electrostatic precipitators due to the small particle size of metal-containing particulates.
- o Non-volatile metals (copper) tend to remain in the soil when exposed to thermal destruction; however, they may slag and foul the equipment.

### DECHLORINATION

#### Principle of Operation

- o Dechlorination is a destruction process that uses a chemical reaction to replace chlorine atoms in the chlorinated aromatic molecules with an ether or hydroxyl group. This reaction converts the more toxic compounds into less toxic, more water-soluble products. The transformation of contaminants within the soil produces compounds that are more readily removed from the soil. An evaluation of the end products is necessary to determine whether further treatment is required.

#### Effectiveness on Organics

- o PCBs, dioxins, furans, and other aromatic compounds (such as pentachlorophenol) have been dechlorinated to approximately 80% removal, with more recent data indicating that removal efficiencies may approach 99.9%.
- o Other limited laboratory data suggest potential applicability to other halogenated compounds including straight-chain aliphatics (such as 1,2-dichloroethane). The removal indicated by the data may be due in part to volatilization.
- o Although no data were available for halogenated cyclic aliphatics (such as dieldrin), it is expected that dechlorination will be effective on these compounds as well.
- o When non-halogenated compounds are subjected to this process, volatilization may occur.

### Effectiveness on Inorganics

- o Dechlorination is not effective on metals, and high concentrations of reactive metals (such as aluminum), under very alkaline conditions, hinder the dechlorination process.

### BIOREMEDIATION

#### Principle of Operation

- o Bioremediation is a destruction process that uses soil microorganisms including bacteria, fungi, and yeasts to chemically degrade organic contaminants.

#### Effectiveness on Organics

- o Bioremediation appears to successfully treat many halogenated aliphatic compounds (1,1-dichloroethane), non-halogenated aromatics (benzene), heterocyclics (pyridine), and other polar compounds (phenol) with removal efficiencies in excess of 99%; however, the high removal implied by the available data may be a result of volatilization in addition to bioremediation.
- o More complex halogenated (4-4' DDT), nitrated (triazine), and polynuclear aromatic (phenanthrene) compounds exhibited lower removal efficiencies, ranging from approximately 50% to 87%.
- o Poly-halogenated compounds may be toxic to many microorganisms.

#### Effectiveness on Inorganics

- o Bioremediation is not effective on metals.
- o Metal salts may be inhibitory or toxic to many microorganisms.

### LOW TEMPERATURE THERMAL DESORPTION

#### Principle of Operation

- o Low temperature thermal desorption is a physical transfer process that uses air, heat, and/or mechanical agitation to volatilize contaminants into a gas stream, where the contaminants are then subjected to further treatment. The degree of volatility of the compound rather than the type of substituted group is the limiting factor in this process.

### Effectiveness on Organics

- o Removal efficiencies have been demonstrated by these units at bench, pilot, and full scales, ranging from approximately 65% for polynuclear aromatics (naphthalene), to 82% for other polar organics (acetone) and 99% for non-polar halogenated aromatics (chlorobenzene).

### Effectiveness on Inorganics

- o Low temperature thermal desorption is not generally effective on metals.
- o Only mercury has the potential to be volatilized at the operating temperatures of this technology.

## CHEMICAL EXTRACTION AND SOIL WASHING

### Principle of Operation

- o Chemical extraction and soil washing are physical transfer processes in which contaminants are disassociated from the soil, becoming dissolved or suspended in a liquid solvent. This liquid waste stream then undergoes subsequent treatment to remove the contaminants and the solvent is recycled, if possible.
- o Soil washing uses water as the solvent to separate the clay particles, which contain the majority of the contaminants, from the sand fraction.
- o Chemical extraction processes use a solvent which separates the contaminants from the soil particles and dissolves the contaminant in the solvent.

### Effectiveness on Organics

- o The majority of the available soil washing data on organic compounds indicates removal efficiencies of approximately 90% for polar non-halogenated organics (phenol) to 99% for halogenated aromatics (chlorobenzene), with lower values of approximately 71% for PCBs to 82% for polynuclear aromatics (anthracene).
- o The reported effectiveness for these compounds could be due in part to volatilization for compounds with higher vapor pressures (such as acetone).

- o This process is least effective for some of the less volatile and less water soluble aromatic compounds.

#### Effectiveness on Inorganics

- o The chemical extraction process, with optimized solvent selection, has demonstrated removal efficiencies of 85% to 89% for volatile metals (lead) and non-volatile metals (copper), respectively.

### IMMOBILIZATION

#### Principle of Operation

- o Immobilization processes reduce the mobility of contaminants by stabilizing them within the soil matrix, without causing significant contaminant destruction or transfer to another medium.
- o Volatile organics will often volatilize during treatment, therefore an effort should be made to drive off these compounds in conjunction with an emission control system.

#### Effectiveness on Organics

- o Reductions in mobility for organics range from 61% for halogenated phenols (pentachlorophenol) to 99% for polynuclear aromatic compounds (anthracene).
- o Immobilization is also effective (84% reduction) on halogenated aliphatics (1,2-dichloroethane).
- o Some organic mobility reductions of the more volatile compounds may actually be removals as a direct result of volatilization during the exothermic mixing process and throughout the curing period.
- o The immobilization of organics is currently under investigation, including an evaluation of the applicability of analytical protocols (EP, TCLP, total analysis) for predicting long-term effectiveness of immobilization of organics. The preliminary available data indicate that significant bonding takes place between some organic contaminants and certain organophilic species in the binding matrix; however, immobilization may not effectively stabilize some organic compounds, such as volatile organics.

## Effectiveness on Inorganics

- o Immobilization can accomplish reductions in mobility of 81% for non-volatile metals (nickel) to 93% for volatile metals (lead).

The effectiveness of the six technologies to treat soil was classified as having demonstrated effectiveness, potential effectiveness, or no expected effectiveness for the eleven contaminant groups (Figure 2). The ratings were based on removal efficiency, scale of operation, and potential for adverse effects as follows:

- o **Demonstrated Effectiveness:** A significant percentage of the data, at least 20%, is from pilot or full scale operations, the average removal efficiency for all of the data exceeds 90%, and there are at least ten data pairs.
- o **Potential Effectiveness:** The average removal efficiency for all of the data exceeds 70%.
- o **No Expected Effectiveness:** The average removal efficiency for all of the data is less than 70% and no interference from the contaminants in the soil is expected.
- o **No Expected Effectiveness:** Potential adverse effects to the environment or the treatment process may occur. For example, high concentrations of metals may interfere with biological treatment.

In some cases, a different rating was selected when additional qualitative information and engineering judgment warranted. Two ratings were selected if the compounds within a treatability group were so variable that a range of conclusions could be drawn for a particular technology.

Although some of the data upon which the analysis is based have limited quality assurance information, the data, nevertheless, do indicate potential effectiveness (at least 90% to 99% reduction of concentration or mobility of hazardous constituents) of treatment technologies to treat Superfund wastes. Some reductions in organic concentrations or organic mobility of more volatile compounds may actually represent the removal of those compounds as a direct result of volatilization. Technologies where this is most likely to occur include dechlorination, bioremediation, soil washing, or immobilization, and consideration of appropriate emission controls is required. Percentage removal reductions (removal efficiencies) are not always a good measure of effectiveness, especially when high

TECHNOLOGY TREATABILITY GROUP	THERMAL DESTRUCTION	DECHLORINATION	BIOREMEDIATION <sup>4</sup>	LOW TEMPERATURE THERMAL DESORPTION	CHEMICAL EXTRACTION AND SOIL WASHING	IMMOBILIZATION <sup>4</sup>
NON-POLAR HALOGENATED AROMATICS (W01)	●	●	● <sup>3</sup>	● ●	●	●
PCBs, HALOGENATED DIOXINS, FURANS, AND THEIR PRECURSORS (W02)	●	●	● <sup>3</sup>	● <sup>1</sup>	●	● <sup>1</sup>
HALOGENATED PHENOLS, CRESOLS, AMINES, THIOLS, AND OTHER POLAR AROMATICS (W03)	● <sup>3</sup>	●	●	●	●	● <sup>3</sup>
HALOGENATED ALIPHATIC COMPOUNDS (W04)	●	● <sup>2</sup>	● <sup>2</sup>	●	●	● <sup>2</sup>
HALOGENATED CYCLIC ALIPHATICS, ETHERS, ESTERS, AND KETONES (W05)	●	● <sup>1</sup>	● <sup>1</sup>	○ <sup>1</sup>	● <sup>1</sup>	● <sup>1</sup>
NITRATED COMPOUNDS (W06)	●	○ <sup>1</sup>	●	○ <sup>1</sup>	●	● <sup>1</sup>
HETEROCYCLICS AND SIMPLE NON-HALOGENATED AROMATICS (W07)	●	○ <sup>2</sup>	● <sup>2</sup>	●	●	● <sup>2</sup>
POLYNUCLEAR AROMATICS (W08)	●	○ <sup>2</sup>	●	○	●	●
OTHER POLAR NON-HALOGENATED ORGANIC COMPOUNDS (W09)	●	○ <sup>2</sup>	● <sup>2</sup>	●	●	● <sup>2</sup>
NON-VOLATILE METALS (W10)	○ <sup>1</sup>	○ <sup>1</sup>	○X <sup>1</sup>	○ <sup>1</sup>	●	● <sup>3</sup>
VOLATILE METALS (W11)	X <sup>1</sup>	○ <sup>1</sup>	○X <sup>1</sup>	○ <sup>1</sup>	●	●

- Demonstrated Effectiveness
- Potential Effectiveness
- No Expected Effectiveness (no expected interference to process)
- X No Expected Effectiveness (potential adverse effects to environment or process)

- 1 Data were not available for this treatability group. Conclusions are drawn from data for compounds with similar physical and chemical characteristics.
- 2 High removal efficiencies implied by the data may be due to volatilization or soil washing.
- 3 The predicted effectiveness may be different than the data imply, due to limitations in the test conditions.
- 4 These technologies may have limited applicability to high levels of organics.

Figure 2. Predicted Treatment Effectiveness for Contaminated Soil

concentrations remain in the residuals. Some of the performance observations are based upon a relatively small number of data points and may not extrapolate well to the broad array of soils requiring treatment.

## QUANTIFYING TECHNOLOGY EFFECTIVENESS AND LIMITATIONS

### TECHNOLOGY LIMITATIONS

A variety of potential limitations to the effective treatment of Superfund wastes were identified in the analyses of data from OERR's original survey. The EPA offices of OERR, OSW, TIO, and ORD are now working together to identify technology limitations and their impact on technology effectiveness.

The data suggest that the treatment of soil and debris with organic contamination, by technologies other than thermal destruction, will not be able to consistently achieve BDAT standards previously developed for industrial process wastes. The difficulty in treating soil and debris is a direct result of the levels of contaminants, the types/combinations of contaminants, the type of matrix, particle size, and other physical and chemical characteristics of the soil and debris.

The residual concentrations in contaminated soil treated by technologies other than thermal destruction is highly dependent upon the concentrations in the untreated soil. Therefore, when evaluating technologies other than thermal destruction, the ability of those technologies to treat high concentrations of organics should be considered. The number and types of contaminants must also be carefully screened. Organic and inorganic contaminants may require different treatment technologies, thus requiring a treatment train. In some cases, different technologies may be necessary for soils and sludges. In addition, the distribution of contaminants often is also very non-homogeneous and is dependent on patterns of contaminant deposition and transport.

The complex nature of solid waste matrices, such as contaminated soil from a Superfund site, severely complicates the treatment process. Soil is a non-homogeneous living medium, and the proportion of clay, organic matter, silt, sand, debris, and other constituents can affect the treatability of a contaminated soil. For example, the complex bonding forces that are exhibited by various soil fractions, particularly clays and organic matter, can be difficult to counteract and can affect the treatability of contaminated soil. To further complicate these circumstances, the age of many of these sites has allowed significant opportunity for environmental weathering of the contaminants and the medium.

Collectively, these conditions make the treatment of contaminated soil, "old" sludge, and debris a formidable technical challenge. EPA intends to quantify the effects of these factors, and the approach is to analyze the existing treatment data for the effects of these factors. Specific parameters affecting performance will be identified from existing data; parameters include: soil morphology (particle size distribution), clay content, permeability, total organic carbon, cation exchange capacity and as many as twenty other parameters. Differences in treatment performance among different technologies, contaminants and soil and debris types will be investigated.

#### DATA COLLECTION

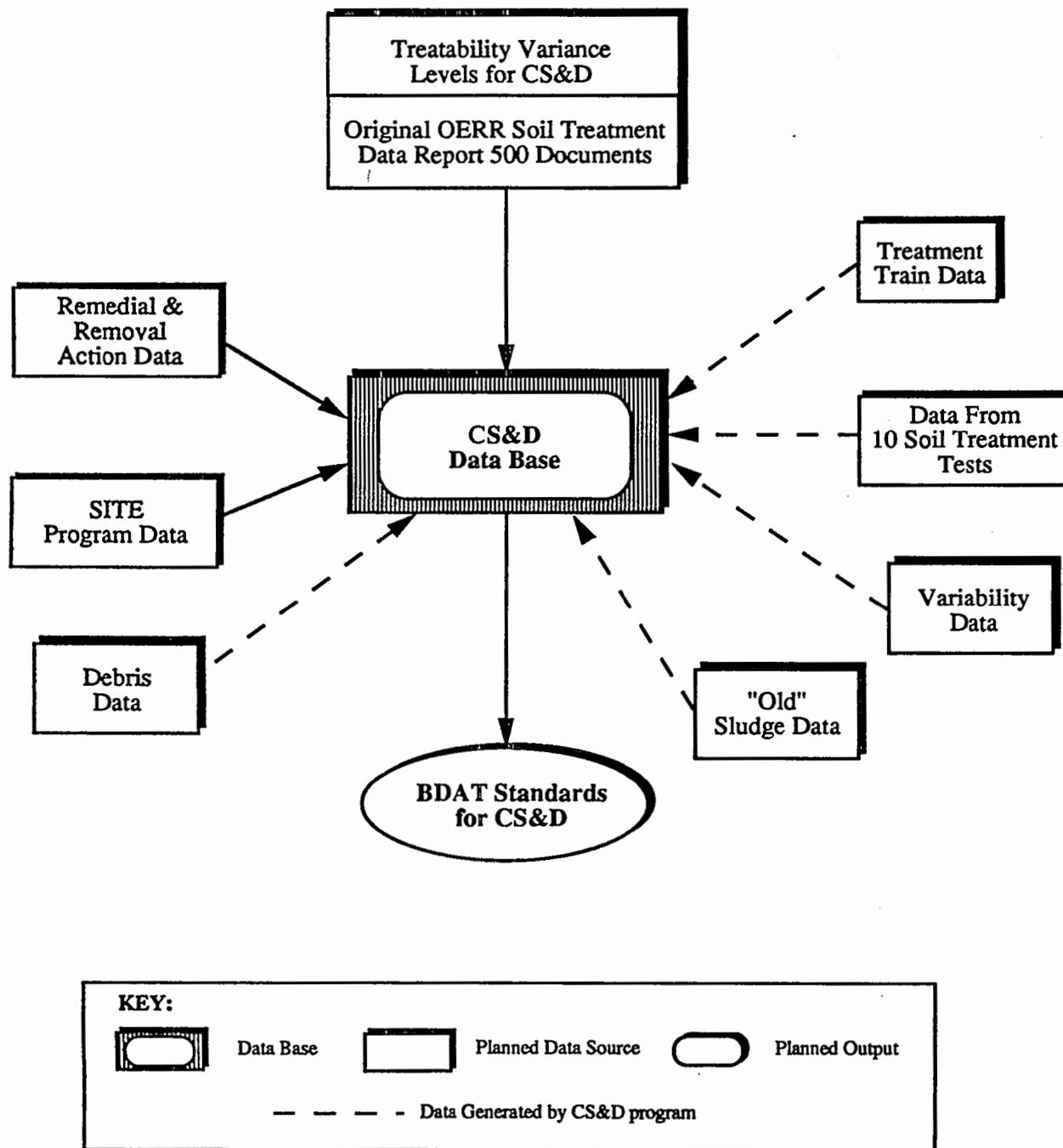
EPA is in the process of developing the final regulations for contaminated soil and debris. The initiatives EPA has taken involve collecting all existing information on the treatment of soil and debris to supplement the first data collection effort and conduct experimental tests, when necessary, to better understand the process (Figure 3). The EPA offices of OERR, OSW, TIO, and ORD are working together in these efforts due to the complexity of developing standards for soil and debris. Discussion of the initiatives follows.

#### Existing Data Collection

The targets for existing soil and debris treatment data include recent remedial/removal actions, Department of Defense (DOD) and Department of Energy (DOE) actions, Superfund Innovative Technology Evaluation (SITE) program demonstrations, and activities conducted by private research organizations and vendors. The information that is being requested includes data on performance as well as other information important for technology transfer. Parameters of interest include: contaminants treated, scale of the test, measured contaminant concentrations before and after treatment, QC protocols, design and operating parameters of the treatment system, methods to improve performance and problems encountered in treatment. The information that is collected will be entered in the soil and debris data base, designed specifically for storing and managing this information.

#### Soil Treatment Tests

The treatment tests that are being performed are tests on contaminants and technologies that lacked adequate treatment performance data, but would be available technologies for treating contaminated soil and debris (CS&D). Ten treatment tests are planned; the technologies that will be tested include bioremediation, low temperature thermal desorption, chemical



**Figure 3. Development Of LDRs For CS&D Data Collection Approach**

extraction, soil washing, and stabilization. The technologies will be applied to different types of soils and contaminants. For example, the biotreatment tests will be conducted on three soil types with soil classifications ranging from sandy to clayey. In addition, different types of contaminants, including soils high in PNAs, PCBs and metals, will be tested. The stabilization technology will be tested as both a primary technology and as a residual treatment.

The treatability tests will be conducted according to the OSW "Quality Assurance Program Plan for Characterization Sampling and Treatment Tests Conducted for the Contaminated Soil and Debris Program" (5) and site specific Sampling and Analysis Plans. The individual sampling plans specify holding times, analytical methods, chain of custody, and quality control measures, such as blanks and spikes. The tests will include measurements of contaminant concentrations before and after treatment, and measurements of the waste characteristics that affect the performance of soil treatment technologies. Examples of waste characteristics that affect treatment performance include but are not limited to moisture content, oxidation/reduction potential, and particle size distribution; the parameters that affect performance are listed in the QA Program Plan.

#### Treatment Trains

OERR recognizes that much of the soil and debris from Superfund sites are mixtures of contaminants and that individual contaminants may need to be treated differently. Treatment trains may be utilized in these cases. EPA wants to know the types of technologies applied to mixtures of contaminants and the effectiveness of the system. The major source of this type of data will be from existing data, however, several of the treatment tests will involve treatment trains. The treatment trains used in the tests will be a technology for treating the organic contaminants and stabilization/solidification to treat the inorganics (metals) remaining in the soil residues.

#### Debris Treatment

Parallel with the effort to collect data on soil is an effort to collect existing information on the treatment of debris. The first data collection effort obtained very limited data on debris treatment. The studies indicated that debris could constitute as much as fifty percent of the contaminated media, such as might be found at a wood preserving site. OERR also recognized that the sampling procedures used to provide representative samples of debris contamination were not well documented. Recognizing the importance of debris, the CS&D Program has implemented a comprehensive review of debris

sampling, analysis and treatment. The treatment technologies that require treatment performance data will be tested by the CS&D Program. The characteristics of debris that have been determined to affect treatment include permeability and destructibility. The potential treatment technologies that have been identified for debris to date are destruction, chemical extraction, physical removal, and sealing/solidification.

### "Old" Sludge

The OERR data survey identified the existence of large quantities of "old" sludges on Superfund sites. These sludges have aged or weathered, and are different than typical RCRA sludges. The data on "old" sludge indicated that sludges are not consistently defined in the literature. Furthermore, these sludges, when identified, had higher concentrations of contaminants than soils, and as a result, did not meet treatability variance levels as frequently as soil. Of the OERR survey data, 55% of the sludge treatment tests met variance levels, while 78% of the soil treatment tests met variance levels. These results indicate that sludge may require separate treatment standards. In order to quantify the treatability of sludges for regulatory development purposes, more data will be collected on the characteristics and treatability of sludges. Existing data will be collected as part of the data collection effort, and characterization tests will be conducted on sludges from Superfund sites to obtain the physical and chemical characteristics of "old" sludge.

### Variability Factors

#### Soil Morphology

Because the variability of the soil matrix may have significant effects on the ability of a technology to perform, EPA is conducting a special project to test the effects of soil morphology or composition on treatment technology performance. Preliminary data indicate that clayey soils are treated less effectively than silty or sandy soils by some technologies. To evaluate this finding, experimental treatment tests will be conducted on three different soil types - sandy, silty, and clayey. Each soil type will be subjected to low temperature thermal desorption, solvent extraction, and solidification/stabilization. Data generated in this study and the available treatment data will be used to develop a correlation between soil type and treatment effectiveness.

#### Materials Handling, Preprocessing and Treatment

Additional factors influencing treatment performance involve materials handling, pretreatment processing, and design and

operation of the treatment system. The previous OERR data survey indicated that all three of these factors can have important effects on treatment performance and therefore they are being evaluated in the current study.

A critical element in soil treatment is materials handling. Special approaches to waste transfer throughout the treatment system are particularly important for solids and viscous sludges, where traditional conveyance methods are frequently ineffective. Slugs of material or debris tend to jam treatment equipment, resulting in breakage, downtime, and the potential for uncontrolled releases to the environment.

The preprocessing of waste to maximize homogeneity and modify the waste characteristics is also important to successful treatment technology operation. Any treatment technology will operate most efficiently and cost effectively when it is designed and utilized to treat a homogeneous waste with a narrow range of physical/chemical characteristics. If contaminant types and concentrations, waste viscosity, BTU content, moisture content, acidity, alkalinity, etc. vary widely, control of the system can be difficult and costly to maintain. Many of these waste characteristics can be modified and improved with appropriate preprocessing.

In addition, the most effective technology performance is achieved when the soil particle size is small and the maximum amount of surface area is exposed. This condition facilitates adequate contact between the contaminant sorption sites and the driving force of the technology (i.e., microorganism, solvent, warm air, etc.). The key to achieving this contact, and subsequent contaminant destruction, transfer to another medium, or bonding, is often achieved only through significant preprocessing.

Materials handling and preprocessing technologies with potential application to contaminate soil are currently in use in industries such as construction, agriculture, and mining. All of these industries routinely handle large quantities of soil or rock. The use of technologies from these industries should be considered during all soil remediation activities. Materials handling and preprocessing techniques should also be incorporated in treatability testing programs. The results of such tests will better define the range of waste characteristics which the full-scale technology will have to treat.

EPA is obtaining results on preprocessing effects from mixing studies performed on various uncontaminated soils. The tests are designed to quantify the mixing of soil and test the effects of soil homogeneity on treatment performance. A selection of soil types and physical conditions will be combined

to provide a matrix of samples commonly encountered during treatment. Mixing experiments will be conducted on uncontaminated soil at three scales (bench, pilot and full) to establish trends in the degree of mixing as a function of soil type, physical condition, and scale. Similarly, treatment tests will be performed on contaminated soil at the bench and pilot scale on a select set of samples from this matrix. Data generated from the treatment tests could be used to establish a correlation between treatment effectiveness and degree of mixing.

## CONCLUSIONS

EPA has launched a comprehensive and aggressive effort to develop LDRs based upon best demonstrated available technologies for treating soil and debris. The technical issues that need to be considered in the development of LDRs for soil and debris have been identified and are being investigated in testing programs and by analyses of existing data.

Timely and complete technology transfer is an important key in collecting data and developing land disposal restrictions for contaminated soil and debris. Therefore, EPA will continue to seek and evaluate all treatment results, and use the results for evaluation for regulatory development and technology transfer. In this vein, the data and conclusions presented in this paper represent the most current information available in the Superfund program. EPA recognizes that with each additional treatment test performed more valuable information will be generated regardless of whether the test was successful or not.

It is important that the research, remediation, and vendor experts have an opportunity to participate in the development of the Land Disposal Restrictions for contaminated soil and debris. Two options exist for this participation. First, EPA requests that all available information on the treatment of contaminated soil, sludges, and debris be forwarded to EPA OERR or to CDM Federal Programs Corporation. Second, EPA plans to publish a Notice of Data Availability in the Federal Register in the spring of 1991. This notice will formally notify the public of EPA's regulatory development approach and request the submission of comments and additional data.

The data, experience, and opinions of members of the hazardous waste treatment community, will be valuable additions to this crucial regulatory development effort. Participation in this process is strongly encouraged and will be greatly appreciated. Please send all available information and any

comments or suggestions to EPA OERR or to CDM Federal Programs Corporation at the following addresses:

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## FATE AND TREATABILITY OF DYES IN WASTEWATER

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### ABSTRACT

The first objective of this study was to determine the partitioning of water soluble azo dyes in the activated sludge process (ASP). Specific azo dyes were spiked at 1 and 5 mg/L to pilot-scale treatment systems with both liquid and sludge samples collected. Samples were analyzed by high performance liquid chromatography (HPLC) with an ultraviolet-visible detector. Of the 18 dyes studied, 11 compounds were found to pass through the ASP substantially untreated, 4 were significantly adsorbed onto the mixed liquor solids (ML), and 3 were apparently biodegraded.

Upon completion of the above study an additional study was begun to determine the fate of C.I. Disperse Blue 79, one of the largest production-volume dyes, and select biodegradation products in a conventionally operated activated sludge process and in an anaerobic sludge digestion system. To achieve this objective, a pilot study was conducted with two continuous-feed pilot-scale wastewater treatment systems, one control and one experimental. The experimental treatment system was fed screened, raw municipal wastewater

dosed with a target concentration of 5 mg/L of active ingredient in the commercial formulation of C.I. Disperse Blue 79 and analyzed for the dye and related compounds. The control system was fed only the screened, raw municipal wastewater. A bench-scale activated sludge system was also operated to assess the fate of dye degradation products arising from the anaerobic digestion of sludges produced in the experimental aerobic treatment system. This system was operated to simulate the recycle of digester supernatant to the head-end of a typical wastewater treatment system.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

The U.S. Environmental Protection Agency's (EPA) Office of Toxic Substances (OTS) evaluates Premanufacture Notification (PMN) submissions under Section 5 of the Toxic Substances Control Act (TSCA). Azo dyes constitute a significant portion of these submissions. Generally, azo dyes contain between one and three azo linkages (-N=N-), linking phenyl and naphthyl radicals that are usually substituted with some combination of functional groups including: amino (-NH<sub>2</sub>); chloro (-Cl); hydroxyl (-OH); methyl (-CH<sub>3</sub>); nitro (-NO<sub>2</sub>); and sulfonic acid, sodium salt (-SO<sub>3</sub>Na). OTS is concerned because some of the dyes, dye precursors and/or their degradation products such as aromatic amines, which are also dye precursors, have been shown to be or are suspected to be, carcinogenic (1).

One aspect of the PMN review process is to estimate the release of a new chemical. The industrial manufacturing and processing of azo dyes generates a wastewater contaminated with azo dyes, which is typically treated in a conventional wastewater treatment system. The effectiveness of this treatment must be known in order to estimate the release from this source. Therefore, EPA's Office of Research and Development undertook a study to determine the fate of specific water soluble azo dye compounds in the activated sludge process (ASP).

The study was approached by dosing the feed to the pilot ASP systems with various water soluble azo dyes and by monitoring each dye compound through the system, analyzing both liquid and sludge samples. The fate of the parent dye compound was assessed via mass balance calculations. These data could determine if the compound was removed by adsorption, apparent biodegradation, or not removed at all. The results for 18 dye compounds tested are presented.

Upon completion of this research a follow-up study was implemented at the request of the TSCA Interagency Testing Committee (ITC). The ITC is comprised eight member agencies which determine areas or chemicals which require investigation under the TSCA. The member agencies are:

- Council on Environmental Quality;
- Department of Commerce;
- Environmental Protection Agency;
- National Cancer Institute;
- National Institute of Environmental Health Sciences;
- National Institute for Occupational Safety and Health;
- National Sciences Foundation; and
- Occupational Safety and Health Administration.

The ITC requested that C.I. Disperse Blue 79 be investigated because of "The lack of measured values on physical and chemical properties for C.I. Disperse Blue 79 increases the uncertainty with respect to chemical fate predictions . . . Disperse Blue 79 released to the environment is likely to partition to both water and sediments. In sediments, it may degrade anaerobically and release 2-bromo-4,6-dinitroaniline. No data have been found to substantiate or refute these predictions. Since the dye has widespread large use in the United States and is likely to be released to the environment during both manufacture and use, it is recommended that biodegradation studies be conducted to determine (1) the potential for aerobic and anaerobic biodegradation, and (2) the identity of relatively persistent intermediates, if any, resulting from biodegradation" (2).

The purpose of this study was to determine the fate of C.I. Disperse Blue 79 and select biodegradation products in a conventionally operated ASP and in an anaerobic sludge digestion system. Two continuous-feed, pilot-scale wastewater treatment systems (one control and one experimental) were operated at the Milwaukee Metropolitan Sewerage District South Shore Wastewater Treatment Plant. In addition to these pilot-scale systems, a bench scale activated sludge system was operated to assess the fate of dye degradation products from a digester in an anaerobic treatment system. This system was operated to simulate the recycle of digester supernatant to the head-end of a typical wastewater treatment system.

#### FATE STUDY FOR VARIOUS AZO DYES

##### EXPERIMENTAL PROGRAM

Screened raw wastewater from the Greater Cincinnati Mill Creek Sewage Treatment Plant was used as the influent (INF) to three pilot-scale activated sludge biological treatment systems (two experimental and one control) operated in parallel. A diagram of an aerobic system is presented in Figure 1. The system used for this study did not include the thickening or digester stages that are pictured as part of the anaerobic treatment system used to study Disperse Blue 79. Each system consisted of a primary clarifier (33 L), complete-mix aeration basin (200 L), and a secondary clarifier (32 L). Each water soluble dye was dosed as commercial product to the screened raw wastewater for the two experimental systems operated in parallel at targeted active ingredient doses of 1 and 5 mg/L of influent flow (low and high spike systems, respectively). The principal focus of this work was on the ASP, and, as such, the primary sludge was not sampled.

FIGURE 1. AEROBIC AND ANAEROBIC TREATMENT SYSTEM

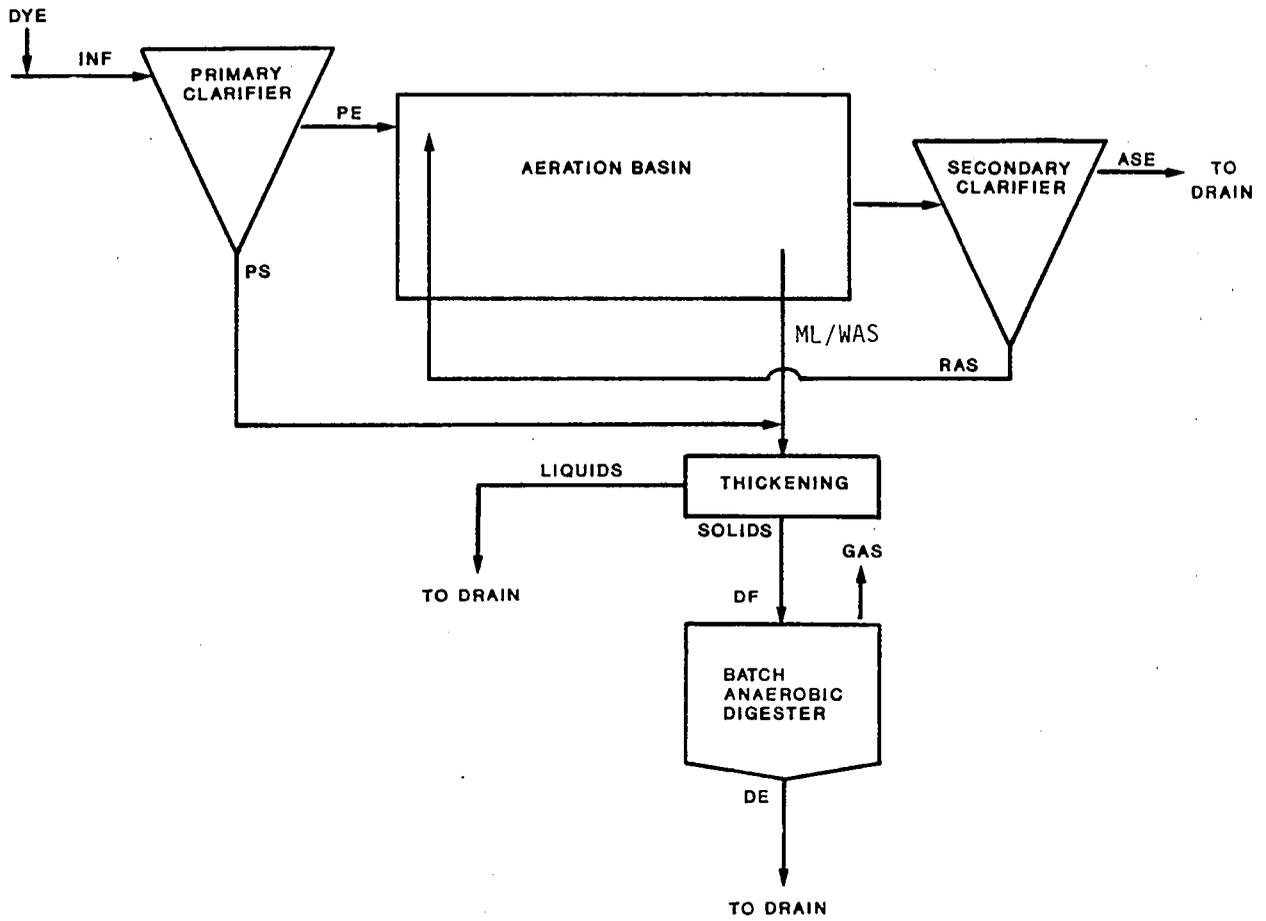


Table I presents a summary of the average operating conditions of the pilot plant systems.

TABLE 1. SUMMARY OF OPERATING CONDITIONS

Parameter	Value
Influent flow rate, L/d	720
Primary sludge flow rate, L/d	6
Primary effluent flow rate, L/d	714
Mixed liquor wastage flow rate, L/d	67
Secondary effluent flow rate, L/d	647
Solids retention time, days	2.7
Hydraulic retention time, days	0.28
Dissolved oxygen, mg/L	2.0-4.0
Target influent spike dosages, mg/L	
Low	1
High	5
Influent pH, pH units	7.0-8.0
Aeration basin temperature, °C	21-25

Before each data collection phase, dye analytical recovery studies were conducted by dosing the purified dye compound into organic-free water, influent wastewater, and mixed liquor. These studies were run in duplicate and each recovery study was repeated at least once to ensure that the dye compound could be extracted. Purified dye standards were analytically prepared from the commercial dye product by repeated recrystallization. The analytical technique used to recover the dye from each source is presented in reference 3.

All systems were operated for at least three times the solids retention time to ensure acclimation prior to initiation of data collection. All samples were 24 hr composites made up of 6 grab samples collected every 4 hr and stored at 4°C. The 18 water soluble, acid and direct azo dyes studied are listed below in Table 2 by Colour Index (4) name and number.

## RESULTS AND DISCUSSIONS

Before a compound was judged acceptable for testing, spike recovery studies were performed for each dye. The recoveries for all 18 dyes were generally very good and with low standard deviations. Recovery for most dyes was within 80% and 120%; thus, it appeared little or no chemical transformation was occurring. The spike recovery method and results are available in reference 3.

TABLE 2. DYE COMPOUNDS SPIKED TO THE ACTIVATED SLUDGE PROCESS

Colour Index Name	Colour Index Number
C.I. Acid Black 1	20470
C.I. Acid Blue 113	26360
C.I. Acid Orange 7	15510
C.I. Acid Orange 8	15575
C.I. Acid Orange 10	16230
C.I. Acid Red 1	18050
C.I. Acid Red 14	14720
C.I. Acid Red 18	16255
C.I. Acid Red 88	15620
C.I. Acid Red 151	26900
C.I. Acid Red 337	----- *
C.I. Acid Yellow 17	18965
C.I. Acid Yellow 23	19140
C.I. Acid Yellow 49	18640
C.I. Acid Yellow 151	13906
C.I. Direct Violet 9	27885
C.I. Direct Yellow 4	24890
C.I. Direct Yellow 28	19555

\*Not assigned as of 01/91. Chemical Abstracts Number = 67786-14-5.

In addition to the spike recovery study, no photodegradation of the dyes was found in laboratory studies. Moreover, the estimated Henry's law constant for each dye tested was less than  $10^{-15}$  atm-m<sup>3</sup>/mol, and, as such, air stripping was very unlikely (5). Therefore, adsorption and/or biodegradation appeared to be the only removal mechanisms.

Eleven of the 18 azo dyes studied passed through the ASP substantially untreated with the data from the low and high spike systems in excellent agreement for these dyes. These were:

C.I. Acid Black 1	C.I. Acid Yellow 17
C.I. Acid Orange 10	C.I. Acid Yellow 23
C.I. Acid Red 1	C.I. Acid Yellow 49
C.I. Acid Red 14	C.I. Acid Yellow 151
C.I. Acid Red 18	C.I. Direct Yellow 4
C.I. Acid Red 337	

The relatively high sulfonic acid substitution of these dyes may explain why they were not removed. If the azo dye has high sulfonic acid substitution, then little or no adsorption of the dye by the microbial cell or cell byproducts would occur, thus limiting the chance of aerobic biodegradation (6). Ten of the 11 above dyes have at least two sulfonic acid functional groups, C.I. Acid Red 337 has one.

The positioning of the sulfonic acid functional group(s) and the molecular weight of the compound also appeared to have an affect on how the compound partitions. Four compounds were adsorbed onto the WAS and apparently not biodegraded. These were:

C.I. Acid Blue 113  
C.I. Acid Red 151  
C.I. Direct Violet 9  
C.I. Direct Yellow 28

C.I. Acid Blue 113, C.I. Acid Red 151, and C.I. Direct Violet 9 represent three of the four diazo (two azo bonds) structures. Although these dyes are sulfonated compounds with two of the three having two sulfonic acid functional groups, they also have a greater molecular weight than the other compounds. Further investigations into the effect of sulfonation (both in number of groups and position) versus molecular weight are necessary before a relationship, if any exists, could be developed.

Three compounds appeared to be biodegraded. These were:

C.I. Acid Orange 7  
C.I. Acid Orange 8  
C.I. Acid Red 88

The conclusion that these compounds were apparently biodegraded comes from an inspection of the mass balance data (3); for each compound, very little of the dye was recovered during sampling. However, the preliminary recovery studies showed that the compound could be recovered without difficulty from wastewater and sludge matrices. Since the compounds were not found in the activated sludge effluent (ASE) or mixed liquor solids (ML), samples and chemical transformation appeared not to be occurring, then biodegradation would account for the apparent loss of the parent compound. The partitioning of the dye between the influent (INF), primary effluent (PE), ASE, and ML along with the mass balance data summary for each dye are available in reference 3.

In addition to the 18 dyes thus far discussed, 11 other azo dyes were investigated during this study but the analytical recovery methodology did not produce satisfactory recoveries from the various matrices for these dyes. Table 3 identifies these dyes.

TABLE 3. DYE COMPOUNDS NOT TESTED DUE TO POOR RECOVERY

Colour Index Name	Colour Index Number
C.I. Acid Blue 92	13390
C.I. Acid Blue 158	14880
C.I. Acid Brown 14	14720
C.I. Acid Red 114	23635
C.I. Direct Black 80	31600
C.I. Direct Blue 15	24400
C.I. Direct Blue 78	34200
C.I. Direct Blue 80	24315
C.I. Direct Red 24	29185
C.I. Direct Red 80	35780
C.I. Direct Red 81	28160

## FATE OF DISPERSE BLUE 79 IN AEROBIC AND ANAEROBIC TREATMENT

## EXPERIMENTAL PROGRAM

Two pilot-scale treatment systems were operated for the entire study, while only during the later phase was the bench-scale system operated.

Because a reliable method for dye analysis was needed to determine the fate of C.I. Disperse Blue 79 in the treatment system, an analytical procedure was developed. Various extraction methods and solvents were investigated to develop a suitable extraction procedure to prepare samples for high-performance liquid chromatography (HPLC) analysis.

A diagram of the aerobic and anaerobic treatment system used for this study is presented in Figure 1. Both pilot-scale activated sludge systems included a contact tank, a conical-shaped primary clarifier, an aeration basin, and a conical-shaped secondary clarifier. The contact tanks were installed to ensure the dye was mixed with the feed and to obtain a 30-min contact time between the raw wastewater and the dye. The primary and secondary clarifiers were approximately 49 L, and the aeration tanks were approximately 185 L.

The activated sludge basins were separated into three cells to operate as a plug-flow system. Peristaltic pumps supplied the screened, raw wastewater to the contact tanks. Gravity moved the wastewater from the contact tanks to the primary clarifiers, then to the aeration basins, and on to the secondary clarifiers. Activated sludge was wasted from the aeration basins via peristaltic pumps. Primary sludge was wasted manually once each day. The target hydraulic retention time (HRT) in both activated sludge units was 5.5 hr and the solids retention time (SRT), 7 days.

The anaerobic digesters were cylindrical-shaped vessels constructed of clear PVC. Each digester had a total volume of 70 L with an operating volume of 39 L. The digesters were completely mixed and heated to maintain an operating temperature of 35°C. Gas production from the digesters was monitored with gas meters.

Waste activated sludge and primary sludge from each activated sludge unit were mixed, thickened, and fed to the respective anaerobic digesters. The target SRT of the anaerobic digesters was 15 days and the target loading was 1.2 kg total volatile solids (TVS)/m<sup>3</sup>•day.

The experimental treatment systems received screened, raw wastewater dosed with a target concentration of 5 mg/L of the active ingredient in C.I. Disperse Blue 79. The control system received only the screened, raw wastewater. After acclimation and steady state conditions were reached, the following samples from each system were analyzed for the dye and related compounds: INF, PE, ASE, primary sludge, ML, digester feed, digester supernatant, and digester effluent.

The bench-scale system was an activated sludge unit that was fed a mixture of primary effluent from the experimental system, supernatant from digester feed preparation (primary and waste activated sludge thickening), and centrate from centrifuging digested sludge from the anaerobic digester. The mixture was prepared to simulate the recycle of digester supernatant and primary and thickened waste activated sludge supernatant to the head-end of a treatment plant. The activated sludge unit consisted of a 6-L conical reactor, which served as the aeration basin; a 2-L inner cone for solids recycle; and a 125-mL clarifier tube for effluent clarification. Peristaltic pumps were used to deliver the feed and remove waste activated sludge from the unit.

## RESULTS AND DISCUSSION

The recovery of C.I. Disperse Blue 79 was completed by an extraction technique followed by HPLC and spectrophotometric analysis. The recovery of the dye was acceptable and the method and results are presented in reference 7.

Operating and analytical data for the pilot-scale activated sludge units are summarized in Table 4. The data for both Units 1 and 2 were similar. The average final effluent TCOD value for Unit 2 was 73.5 mg/L and that for Unit 1 was 59.2 mg/L. Although the slightly higher effluent TCOD value for Unit 2 may have been caused by adding dye to the unit, the data indicate that the overall performance of the experimental activated sludge system was not affected by this addition.

The anaerobic digester's operating and analytical data are summarized in Table 5. The feed, effluent, and operational data indicate no significant difference between the two units. No adverse affect was detected on the operation of the experimental digester as a result of adding dye.

TABLE 4. SUMMARY OF THE PILOT-SCALE ACTIVATED SLUDGE SYSTEM'S OPERATIONAL AND ANALYTICAL DATA FOR THE DYE TESTING PERIOD

Parameter	Unit 1*	Unit 2†
<u>Feed data</u>		
TSS (mg/L)	238	211
TCOD (mg/L)	364	375
TBOD (mg/L)	182	177
NH <sub>3</sub> -N (mg/L)	22.5	20.7
<u>Operational data</u>		
HRT (hr)	5.28	5.28
SRT (days)	5.94	5.87
<u>Mixed liquor data</u>		
Temperature (°C)	20.0	20.0
pH (range)	6.8-8.0	6.8-7.6
DO, Cell 1 (mg/L)	2.4	2.8
DO, Cell 2 (mg/L)	3.6	3.5
DO, Cell 3 (mg/L)	3.6	3.9
TSS (mg/L)	3,030	3,060
O <sub>2</sub> Uptake rate (mg/L hr)	6.8-8.0	6.8-7.6
SSVI (ml/g)	73.1	58.0
<u>Primary effluent data</u>		
TSS (mg/L)	134	139
NH <sub>3</sub> -N (mg/L)	22.7	21.7
<u>Final effluent data</u>		
TCOD (mg/L)	59.2	73.5
TBOD (mg/L)	16	21
TSS (mg/L)	27	31
NH <sub>3</sub> -N (mg/L)	0.26	0.18

\*Control

†Spiked

TABLE 5. SUMMARY OF THE ANAEROBIC DIGESTER'S OPERATIONAL AND ANALYTICAL DATA FOR THE DYE TESTING PERIOD

Parameter	Unit 1*	Unit 2†
<u>Feed data</u>		
TSS (mg/L)	21,300	21,400
TS (%)	2.42	2.42
TVS (%)	1.81	1.82
<u>Effluent data</u>		
pH (range)	6.6-7.0	6.6-7.0
Temperature (°C)	35.0	35.0
TSS (mg/L)	12,700	12,200
TS (%)	1.46	1.48
TVS (%)	0.94	0.97
<u>Operational data</u>		
Alkalinity (mg/L)	2,930	2,820
Volatile acids (mg/L)	< 51	< 50
Loading (kg TVS/m <sup>3</sup> day)	1.21	1.22
TVS reduction (%)	47.8	46.4
Gas production (m <sup>3</sup> /kg TVS destroyed)	0.76	0.87
Percent CH <sub>4</sub> in gas	58.9	57.9

\*Control

†Spiked

The influent and effluent streams from the experimental activated sludge systems were sampled and analyzed for C.I. Disperse Blue 79 and any related compounds (see reference 7) to determine the fate of the dye in the treatment system. The average dye and TSS concentrations from the Unit 2 samples are summarized in Table 6. Influent and waste mixed liquor samples were analyzed from Unit 1.

The average dye concentration in the Unit 2 feed to the primary clarifier was 4.40 mg/L and the average final effluent concentration was < 0.93 mg/L, so that the average dye removal was greater than 79%. Although 5 of 19 analyzed effluent samples were below the 0.25 mg/L detection limit, the effluent dye concentration varied from < 0.25 mg/L to 3.70 mg/L. The variation in effluent dye concentration may have been caused by the variation in effluent TSS (9 - 72 mg/L) concentration.

TABLE 6. AVERAGE C.I. DISPERSE BLUE 79 AND TSS CONCENTRATION IN THE UNIT 2 EXPERIMENTAL ACTIVATED SLUDGE UNIT SAMPLES

Sample Location	C.I. Disperse Blue 79 (mg/L)	TSS (mg/L)
Feed	4.40	212
Primary effluent	4.71	133
Primary sludge	31.8	14,500
Waste activated sludge	93.5	3,060
Final effluent	< 0.93	28

In developing an analytical procedure (7) for C.I. Disperse Blue 79, it was determined that the dye has a high affinity for the activated sludge solids present in the experimental unit. In fact almost all the dye present in a mixed liquor sample was extracted off the solids (7). The correlation coefficient between TSS and dye concentrations in the Unit 2 effluent was determined to be 0.78. Calculations performed on Table 6 data show that each gram of suspended solids in the waste activated sludge (WAS) contained 30 mg of dye. Since the average final effluent TSS concentration was 28 mg/L, the final effluent dye concentration can be calculated to be 0.84 mg C.I. Disperse Blue 79 per liter (assuming TSS is all WAS). Comparing 0.84 mg dye/L to the measured value of < 0.93 mg dye/L presented in Table 6 indicates that the calculated value is very close to the measured value and supports that the dye has a high affinity for the activated sludge. Lowering the final effluent TSS concentration by improving solids removal in the final clarifier will result in a lower dye concentration in the final effluent.

Mass balance calculations were performed with the use of the measured dye concentrations and measured flow rates for each process stream. Mass balance calculations across the entire activated sludge system showed that an average of 86.5% of the dye contained in the feed stream was accounted for in the effluent streams. The primary sludge contained an average of 3.6% of the dye fed to the system; waste activated sludge, 62.3%; and final effluents, 20.4% (the percentages of the three streams do not equal 86.5% because of rounding off the individual values). Since most of the dye fed to the system was recovered and no other related compounds were detected, it can be concluded that no significant biodegradation of C.I. Disperse Blue 79 occurred in the activated sludge system.

Feed sludge and effluent (digested sludge) samples from both the control and experimental digesters were analyzed for dye content. Detectable concentrations of dye were identified by HPLC-UV in 5 of 10 control-unit feed samples and in 4 of 10 effluent samples. The average concentrations were low, however, at < 1.45 mg/L for the feed samples and

< 1.22 mg/L for the effluent sample. The low level of dye in these control unit samples is negligible when compared with the much higher concentrations of dye in the experimental unit samples.

The average experimental unit feed dye concentration was 443 mg/L, and the average effluent concentration was 7.86 mg/L. On average, 98.2% of the dye contained in the feed sludge was degraded in the anaerobic digester.

Thermospray ionization mass spectrometry was used to identify degradation products of C.I. Disperse Blue 79 in the anaerobic digester effluent. With this ionization technique, the parent dye was observable, but because of the electronegativity of many of the functional groups on the molecule (e.g., NO<sub>2</sub>, Br), the sensitivity of the technique for this compound was poor. Four major degradation compounds were tentatively identified and found in significant amounts in the digester effluent. Their exact identity and amounts have not been verified because appropriate analytical standards were not available. Information about the degradation products is contained in reference 7.

During normal operation of a wastewater treatment system, the supernatant from sludge lagoons or other digester sludge thickening operations is returned to the head-end of the plant for treatment. The bench-scale activated sludge system (Unit 3) was operated to study the fate of dye degradation products from the anaerobic digester in an activated sludge system. The feed for Unit 3 was the supernatant from the sludge thickening operation mixed with centrate from centrifuging digester effluent and primary effluent. The supernatant was added to simulate the effluents produced from thickening waste activated sludge in a typical plant.

The operating and analytical data from Unit 3 are presented in Table 7. The average HRT was 6.04 days, which was slightly higher than the Unit 2 value of 5.28 days; the average SRT for Unit 3 was 4.83 days, which was lower than the Unit 2 average of 5.87 days. The Unit 3 average SRT was lower than the target value of 7 days because of a relatively high average effluent TSS value of 40 mg/L. The bench-scale unit settling performance was more variable than that in the pilot units.

The average effluent TCOD and TBOD values were also higher than the pilot unit values. The higher effluent values probably resulted from the higher TSS levels in the final effluent. The performance of Unit 3 with respect to TSS, TBOD, and TCOD removal was not as good as that of the pilot units but was typical of a bench-scale unit.

Table 8 summarizes the dye data from the bench-scale unit feed, waste activated sludge, and final effluent sample analyses. The average feed dye concentration was 3.43 mg/L and the average effluent concentration was 1.32 mg/L, for a removal efficiency of 62%. The effluent concentration was probably high because of the relatively high TSS concentration in the final effluent.

TABLE 7. SUMMARY OF ACTIVATED SLUDGE UNIT 3'S OPERATIONAL AND ANALYTICAL DATA

Parameter	Average Value
<u>Feed</u>	
TSS (mg/L)	130
TCOD (mg/L)	336
TBOD (mg/L)	158
<u>Operation data</u>	
HRT (hr)	6.04
SRT (days)	4.83
<u>Mixed liquor data</u>	
Temperature (°C)	21.5
pH (range)	6.8-8.1
DO (mg/L)	5.6
TSS (mg/L)	1,650
<u>Final effluent data</u>	
TSS (mg/L)	40
TCOD (mg/L)	116
TBOD (mg/L)	31

TABLE 8. BENCH-SCALE ACTIVATED SLUDGE SYSTEM'S C.I. DISPERSE BLUE 79 ANALYTICAL RESULTS

Sample Location	C.I. Disperse Blue 79 (mg/L)	TSS (mg/L)
Feed	3.43	14.5
Waste activated sludge	37.6	2,150
Final effluent	1.32	53

Mass balance calculations of the dye across Unit 3 showed that an average of 75.3% of the dye fed to the unit was accounted for in the effluents from the unit. The mass balance for Unit 2 showed 86.5% of the dye was recovered. Although the recovery from Unit 3 was slightly lower, it does not appear that significant degradation of the dye occurred in the bench-scale activated sludge system.

Degradation products of C.I. Disperse Blue 79 were also monitored in the influent, effluent, and waste sludge from Unit 3. Because no positive identification was made of the by-products, quantification was not possible. Some general observations can, however, be made concerning the degradation products based on relative amounts. The observed trend indicated that the concentration of these compounds decreased across Unit 3. The final effluent samples always contained the lowest concentrations of the degradation products, but because of limited data, further conclusions cannot be drawn. Further evaluation of the degradation products and their fate in biological treatment systems may be subject for further project work.

## CONCLUSIONS

1. A total of 18 water soluble azo dyes were successfully monitored in wastewater and sludge samples collected from pilot-scale ASP systems. The study of 11 additional dyes was attempted but could not be accomplished due to poor analytical recovery.
2. Increased sulfonation seemed to be a major factor in preventing an azo dye compound from being either apparently adsorbed or biodegraded by the ASP.
3. Of the 18 dyes studied, 11 compounds were found to pass through the ASP substantially untreated, 4 were adsorbed onto the WAS and 3 were apparently biodegraded.
4. The addition of C.I. Disperse Blue 79 did not adversely affect the operation of the pilot activated sludge unit or that of the anaerobic digester. Both the control and experimental activated sludge units produced effluents typical of municipal wastewater treatment systems. The anaerobic digesters achieved volatile solids reductions within the normal operating range for municipal digesters.
5. Little evidence of C.I. Disperse Blue 79 degradation in the activated sludge systems was found. Mass balance calculations showed that, on average, 86.5% of the dye contained in the feed to the system was present in the effluent streams.
6. The majority of the C.I. Disperse Blue 79 fed to the activated sludge system was removed in the waste activated sludge. The average dye mass balance obtained around the system was 86.5%; the dye was partitioned in the effluent streams as follows: 3.6% in the primary sludge, 62.3% in the waste activated sludge, and 20.4% in the final effluent.
7. The C.I. Disperse Blue 79 was degraded in the anaerobic digester. The dye concentration was reduced from an average feed value of 566 mg/L to an average effluent value of 15.0 mg/L, or a 97.4% reduction.

8. Possible degradation products of the dye were detected in the digester effluent. Although some preliminary measurements were made to identify the structure of these compounds, no positive identification or quantification of the compounds was made.
9. Based on limited semi-quantitative results, some of the dye degradation products from the anaerobic digester were destroyed when treated in a bench-scale activated sludge system.

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CARBON-ASSISTED ANAEROBIC TREATMENT OF HAZARDOUS LEACHATES

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ABSTRACT

Two anaerobic granular activated carbon (GAC) expanded-bed bioreactors were tested as pretreatment units for the decontamination of hazardous leachates containing volatile and semivolatile synthetic organic chemicals (SOCs). The different characteristics of the two leachate feed streams resulted in one reactor operating in a sulfate-reducing mode and the second in a strictly methanogenic environment. Both reactors were operated with a 6-hr unexpanded empty-bed contact time and achieved SOC removal acceptable for pretreatment units. In both reactors, the majority of the SOCs were removed by biological activity, with GAC adsorption providing stability to each system by buffering against load fluctuations.

KEY WORDS: leachate, synthetic organic chemicals, anaerobic, activated carbon, sulfate reduction, methanogenic, expanded-bed bioreactor.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

Rainfall and surface runoff infiltrating sanitary and industrial landfills and hazardous waste dump sites are exposed to a complex variety of pollutants. Water percolating through a landfill is contaminated with a number of organic and inorganic compounds, and direct discharge of exiting leachate to municipal wastewater treatment plants can result in inadequate removal of many hazardous substances. Mandated by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), physical, biological, or chemical pretreatment options may be necessary for removing hazardous substances from leachates, depending on site-specific contamination.

Many volatile and semivolatile synthetic organic chemicals (SOCs) used as solvents, degreasers, or components in industrial products are present in leachates originating from hazardous waste sites. These SOCs are often inadequately treated in aerobic wastewater treatment processes as volatiles are subject to air stripping, many semivolatiles simply pass through untreated, and highly chlorinated compounds are difficult to degrade aerobically. Leachate pretreatment alternatives are not well defined because leachate chemical profiles vary significantly from site to site. Leachate quality is affected by a variety of factors, including the material in the fill, the site age, and precipitation and climate patterns (1). These factors not only influence the types and concentrations of hazardous compounds in water percolating through a site, but also determine the amounts of background biodegradable substances in a leachate. This will in turn influence the environment within any biological pretreatment process.

With recent advances in anaerobic biological treatment, many leachates contaminated with SOCs can be successfully pretreated. Although leachates are highly complex and variable, many SOCs commonly found in leachates are partially or completely biodegradable in anaerobic systems (2-11). Also, anaerobic processes are generally effective in treating high strength wastes. The anaerobic granular activated carbon (GAC) expanded-bed bioreactor is an anaerobic pretreatment option that appears to be particularly well suited for treating SOC-contaminated leachates. The combined processes of anaerobic degradation and carbon adsorption provide a means for removing a variety of SOCs during pretreatment. Compounds that resist degradation can be controlled with carbon adsorption and replacement.

In this study, leachates containing a mixture of 14 SOCs were treated with anaerobic GAC expanded-bed bioreactors. SOC influent concentrations were maintained at levels typical of leachates from CERCLA waste sites.

## MATERIALS AND METHODS

Two anaerobic GAC expanded-bed bioreactors were used to treat municipal leachates rendered hazardous by the addition of 14 SOCs. The reactors were operated in parallel using identical mechanical feed systems and piping

networks. The treatment systems were operated at the U.S. EPA Test and Evaluation Facility in Cincinnati, Ohio. A schematic representative of the two treatment systems is shown in Figure 1.

#### EXPANDED-BED REACTORS

Each expanded-bed reactor consisted of a 10.2-cm ID, 96.5-cm long, jacketed Plexiglas® tube fitted at the top and bottom with headers to convey influent and effluent streams. Warm water was circulated through the jacket surrounding each reactor to maintain each system at 35°C. Each reactor was charged with 1.0 kg of 16X20 U.S. Mesh F400 GAC (Calgon Carbon Corp.), underlain by a bed of graded gravel that served to distribute flow evenly along the reactor cross-section.

Effluent recycle was maintained at a rate sufficient to achieve completely mixed conditions within each reactor and to sustain a bed expansion of approximately 30%.

#### INFLUENT AND EFFLUENT SYSTEMS

Raw municipal leachate was fed to each reactor from a sealed, chilled, mixed, stainless steel reservoir. A positive pressure head (4-8 in. H<sub>2</sub>O) was maintained in each reservoir using a nitrogen gas blanket. The blanket aided leachate feeding by preventing the development of a vacuum in each sealed reservoir and more importantly prevented oxidation of the leachate. Leachate was fed using stainless steel lines, except around feed pumps, and was introduced into each recycle loop on the suction side of each recycle pump.

A stock solution of the SOC's was fed into the suction side of each recycle loop along with the leachate. By pumping the leachate and the SOC solution independently, better spiking control was possible than if the SOC stock was mixed into the leachate feed reservoirs. Also, volatilization and adsorption losses were prevented. The SOC solution was pumped using a syringe pump and gas-tight, volatile organic chemical (VOC) approved, glass syringes with teflon-tipped barrels. Stainless steel tubing was used for all SOC spiking lines.

Effluent from each reactor was collected in a 50-L graduated vessel so that throughput flow (10 L/day at design flow) could be measured accurately without disturbing the system. Off gases were volumetrically measured using wet-tip gas meters connected to the top of each reactor.

#### MUNICIPAL LEACHATES

Raw municipal leachates were obtained periodically from two sanitary landfills operated by the Delaware Solid Waste Authority (DSWA). Both leachates contained background contamination (e.g., COD, metals, sulfate and sulfide sulfur, ammonia nitrogen, and suspended solids) similar to that expected for many hazardous leachates.

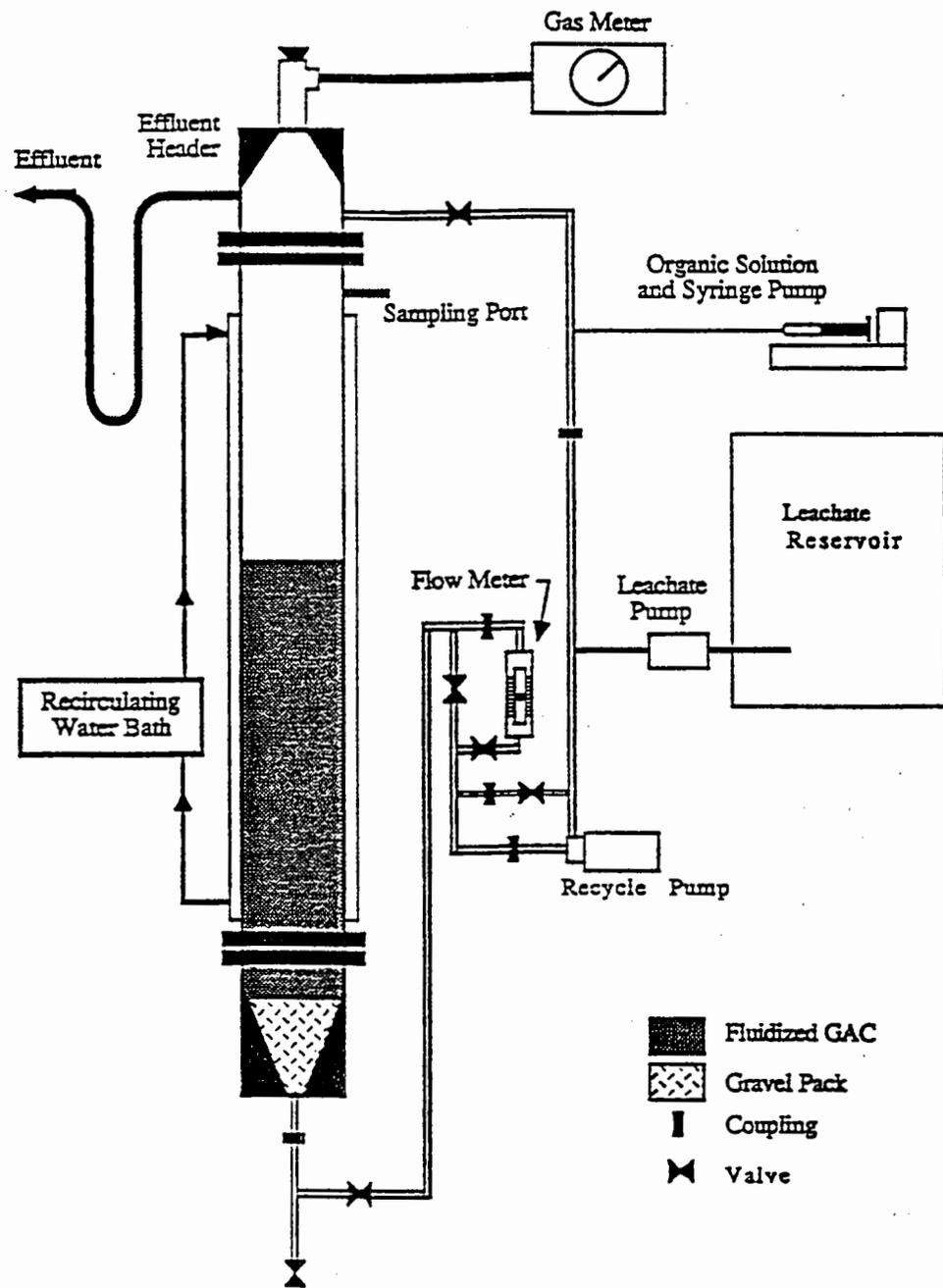


Figure 1. Schematic of Anaerobic GAC Expanded-Bed Treatment System

Reactor A was fed a relatively weak, biologically stabilized leachate (Leachate A) pumped from a collection well at the Cherry Island municipal landfill near Wilmington, DE. This leachate was characterized by low COD levels (approximately 1,100 mg/L) and a low volatile fatty acids (VFAs) content (15% of total COD). Sulfate concentrations averaged 89 mg SO<sub>4</sub>/L. Reactor B received a moderate strength, low sulfate leachate (Leachate B) obtained from the DSWA Southern Solid Waste Facility near Seaford, DE. Leachate B averaged 3,800 mg COD/L, with the majority (60-90%) of the COD comprised of VFAs.

Because of the longer age and accompanying stabilized nature of the landfill that produces Leachate A, COD levels in this leachate were relatively stable over the course of the project (except for one early shipment). Most of the easily biodegradable material in the fill has been consumed, leaving behind a greater fraction of complex refractory compounds such as humic substances. Leachate B COD levels (produced by a younger, less stable landfill) varied significantly, with the highest COD levels occurring in the colder, wetter months. During these months, biodegradation of solubilized organic material is slowed within the landfill and increased flushing rates remove material before it can be consumed internally.

#### SOC SUPPLEMENT

The SOC solution was fed simultaneously with each leachate to obtain leachate contamination levels represented in Table 1. Selection of the nine volatile and five semivolatile SOCs and their corresponding target concentrations was based on a U.S. EPA review of CERCLA leachates (12). Chloroform, although identified as one of the compounds often found in hazardous leachates, was not included in the SOC solution because of its reported toxic/inhibitory effects on anaerobic processes (13).

The SOC solution was prepared in 70-mL batches, and each batch was analyzed several times to ensure that the spike matrix did not change significantly with time. With the particular recipe of compounds used in this project, batches were prepared without the use of a solvent as the compounds were mutually miscible.

#### PROJECT OPERATION

After startup and acclimation (accomplished over 160 days at incremental feed rates of 2 to 10 L/day) to the raw municipal leachates, the leachate flow rate to each reactor was maintained at 10 L/day for the duration of the project. This resulted in an unexpanded empty-bed contact time of 6 hours in each reactor. SOC spiking was initiated at 30% of target levels on Day 67 and was increased to approximately 60% of target levels on Day 105. On Day 133, feed concentrations reached 100% of desired levels. Although the spiking rates were nearly constant during each period, the presence of some SOCs in the raw municipal leachates caused fluctuations in actual compound concentrations, as would be seen in any real hazardous leachate. Throughout the study, the pH in each reactor remained near neutral ranging between 6.8 and 7.2.

Table 1: Typical CERCLA Leachate Profile (1)

<u>Compound</u>	<u>Concentration (<math>\mu\text{g/L}</math>)</u>
VOLATILE ORGANIC COMPOUNDS	
Acetone	10,000
Methyl Ethyl Ketone	5,000
Methyl Isobutyl Ketone	1,000
Trichloroethylene	400
1,1-Dichloroethane	100
Methylene Chloride	1,200
Chlorobenzene	1,100
Ethylbenzene	600
Toluene	8,000
SEMIVOLATILE ORGANIC COMPOUNDS	
Phenol	2,600
Nitrobenzene	500
1,2,4-Trichlorobenzene	200
Dibutyl Phthalate	200
Bis(2-Ethylhexyl)Phthalate	100

Beginning on Day 65, GAC in Reactor A was replaced with prewashed virgin GAC at a rate of 10 g/day (1%/day). This precautionary measure was later deemed unnecessary, and carbon replacement was halted on Day 214. Carbon replacement was not used in Reactor B.

Liquid flow and volumetric off-gas production rates were measured daily. Samples were analyzed weekly for SOCs, total and soluble COD, sulfate, off-gas composition ( $\text{CH}_4$ ,  $\text{CO}_2$ ), metals, ammonia nitrogen, and nitrate nitrogen. VFAs, total and volatile suspended solids (TSS and VSS), and SOCs in the off gas were measured weekly during selected sampling periods.

#### ANALYTICAL METHODS

Isotope dilution analyses of VOCs were carried out according to EPA Method 1624B (14). A Model 5890 Hewlett Packard (HP) gas chromatograph (GC) and a Model 5970 HP mass selective detector were used in conjunction with a Tekmar LSC-2 purge and trap. 5-mL samples containing isotopically-labelled analogs of each of the VOCs were purged (helium, 40 mL/min) for 12 minutes to a Supelco 2-0293 trap. Compounds were desorbed (4.0 min, 210°C) to a packed column (2 m long, 2 mm ID; 1% SP-1000, Carbopak B). The GC column temperature ramped from 45°C to 210°C at 8°C/min. The detector scan range was 35-250 amu with injection and interface temperatures of 210 and 275°C, respectively.

Isotope dilution analyses of the semivolatile compounds were performed according to EPA Method 1625B (14) after continuous liquid-liquid extraction (Method 3520). Isotopically-labelled internal standards were injected into each sample prior to extraction with methylene chloride. The GC (HP Model 5890) was

fitted with a SPB-5 capillary column (30 m long, 0.25 mm ID). The temperature was ramped from 50°C to 280°C at a rate of 8°C/min. The detector (HP Model 5970) scan range was 35-500 amu, with an injection temperature of 270°C and an interface temperature of 280°C.

COD samples were analyzed using COD reagent vials, a block digester, and a spectrophotometer. Prior to analysis, COD samples were acidified and purged with nitrogen to minimize sulfide interference. Sulfate was analyzed by ion chromatography (15), and gas composition was measured using a Fisher 1200 gas partitioner. All other analyses were conducted according to U.S. EPA methods.

All liquid SOC analyses were performed at the U.S. EPA Andrew W. Breidenbach Environmental Research Center (AWBERC). All samples had to be collected, transported to AWBERC, and stored for a short time until analysis. Acidified semivolatile samples were extracted upon arrival at AWBERC. However, volatile samples could not always be analyzed immediately and required a preservation procedure that would allow for some lag time between sample collection and analysis. A VOC sample preservation study, carried out with the analytical support staff of the Risk Reduction Engineering Laboratory, demonstrated that acidified, chilled, VOC samples could be stored for at least 2 weeks without significant losses. In this study, effluent samples (raw leachate feed only) from each reactor were spiked with acetone, methylene chloride, 1,1-dichloroethane (DCA), and toluene at concentrations of 400, 120, 120, and 120 µg/L, respectively. They were acidified and chilled, then analyzed over a period of 2 weeks and compared to a SOC solution made in methanol on the first day. Table 2 shows that the amount of each compound recovered did not vary significantly with time.

Table 2: VOC Preservation Study Results

% Recovery of Analyte Compared to Time Zero  
VOC-Methanol Solution

Day	Methylene Chloride	Acetone	DCA	Toluene
3	94	115	99	101
6	109	138	104	104
8	117	116	102	102
10	102	124	95	110
14	101	128	93	116

## RESULTS AND DISCUSSION

The primary objective in pretreating CERCLA leachates contaminated with SOCs is to remove the hazardous organic compounds before leachates are blended with municipal or industrial wastewater targeted for treatment in aerobic wastewater treatment facilities. However, other contaminants in the leachate need to be at sufficiently low levels so that blended waste streams do not

significantly inhibit the efficiency of aerobic systems. Also, these secondary contaminants, varying with the site-specific nature of each fill, need to be examined as they will strongly influence the pretreatment environment.

#### REACTOR A ENVIRONMENT

The biological activity in Reactor A, treating the weaker strength leachate, was substantially limited by the amount of available substrate entering the reactor. The degradable fraction of the influent COD was consistently low with a VFA content averaging less than 15% of the total COD. With the significant presence of sulfate in this leachate, a competition between methanogens and sulfate-reducing organisms developed. Although biological activity in this reactor was limited, a stable environment persisted throughout the course of the project.

During the entire period of operation at 100% SOC spike levels, Reactor A averaged only 26% COD removal. Until Day 214, carbon replacement accounted for approximately 45% of the COD removal as highly refractory compounds were removed by adsorption. However, after GAC replacement was halted, methane production and sulfate reduction continued to remove the same amount of COD, by mass, as during the period when GAC replacement was practiced. Overall COD removal dropped to an average of 14% with no GAC replacement, but only because the physical removal mechanism of GAC replacement was no longer being used. Although several metals were present in significant amounts, metal toxicity was not observed. Likewise, the SOC's did not appear to inhibit biological activity. Influent and effluent COD concentrations are plotted in Figure 2, and influent and effluent background contaminant concentrations are given in Table 3.

#### REACTOR B ENVIRONMENT

Reactor B, treating the moderate strength leachate, operated principally under methanogenic conditions. During the 100% SOC spiking phase, Reactor B averaged 82% COD removal, with 99% of this converted to methane. COD removal was closely related to the amount of VFAs in the influent leachate. Influent COD levels fluctuated with each leachate shipment, but accompanying responses in methane production indicated a healthy system. As in Reactor A, metal toxicity and SOC inhibition were not observed. Figure 3 shows COD levels entering and exiting Reactor B, and Table 4 lists important influent and effluent background parameter values.

#### SOC REMOVAL

With two uniquely different leachates, SOC removal data can be evaluated for two different anaerobic environments. In both reactors partial or complete mineralization of the hazardous organic compounds appeared to be the predominant removal mechanism, while GAC adsorption provided stability to each system by buffering against loading perturbations until organisms could adapt and respond. Because of the number of compounds being spiked, the length of the project, and the complex nature of each leachate, carbon adsorption could not be the

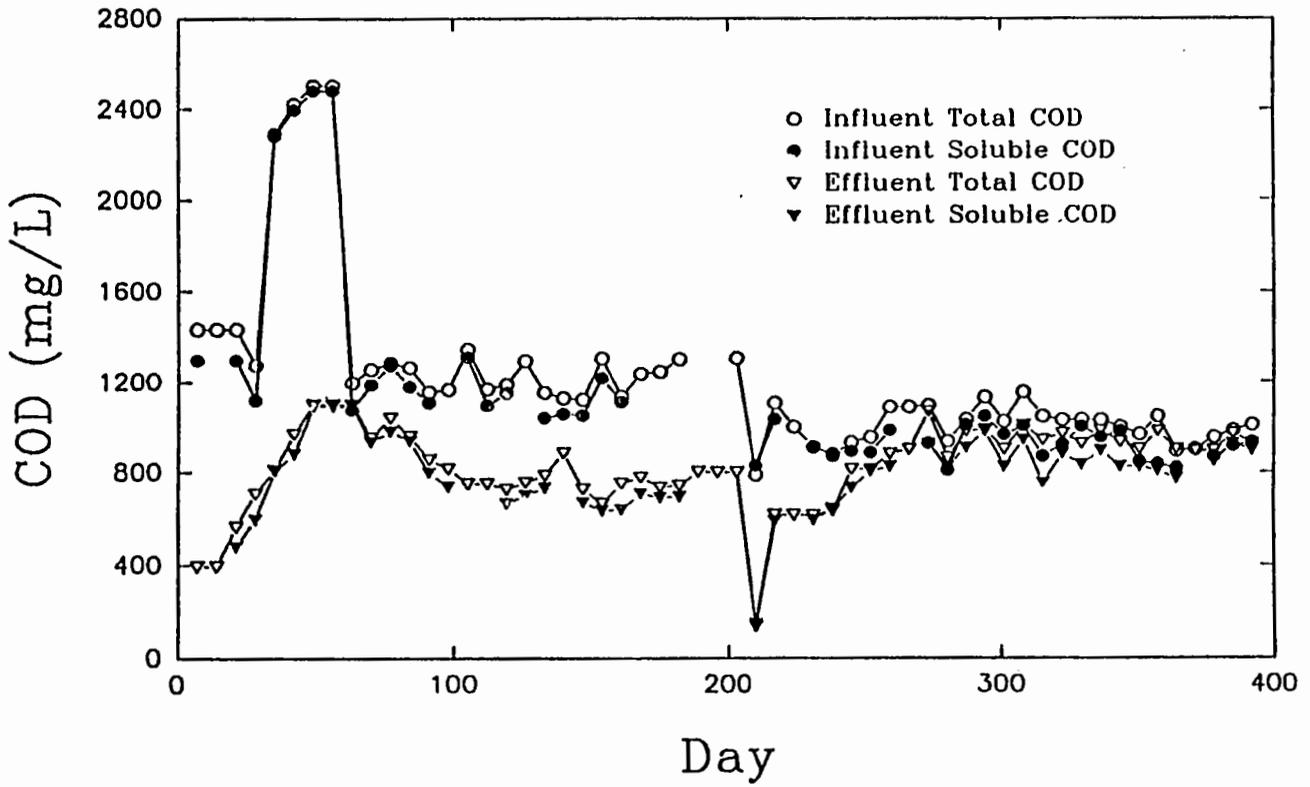


Figure 2: Influent and Effluent COD Concentrations for Reactor A.

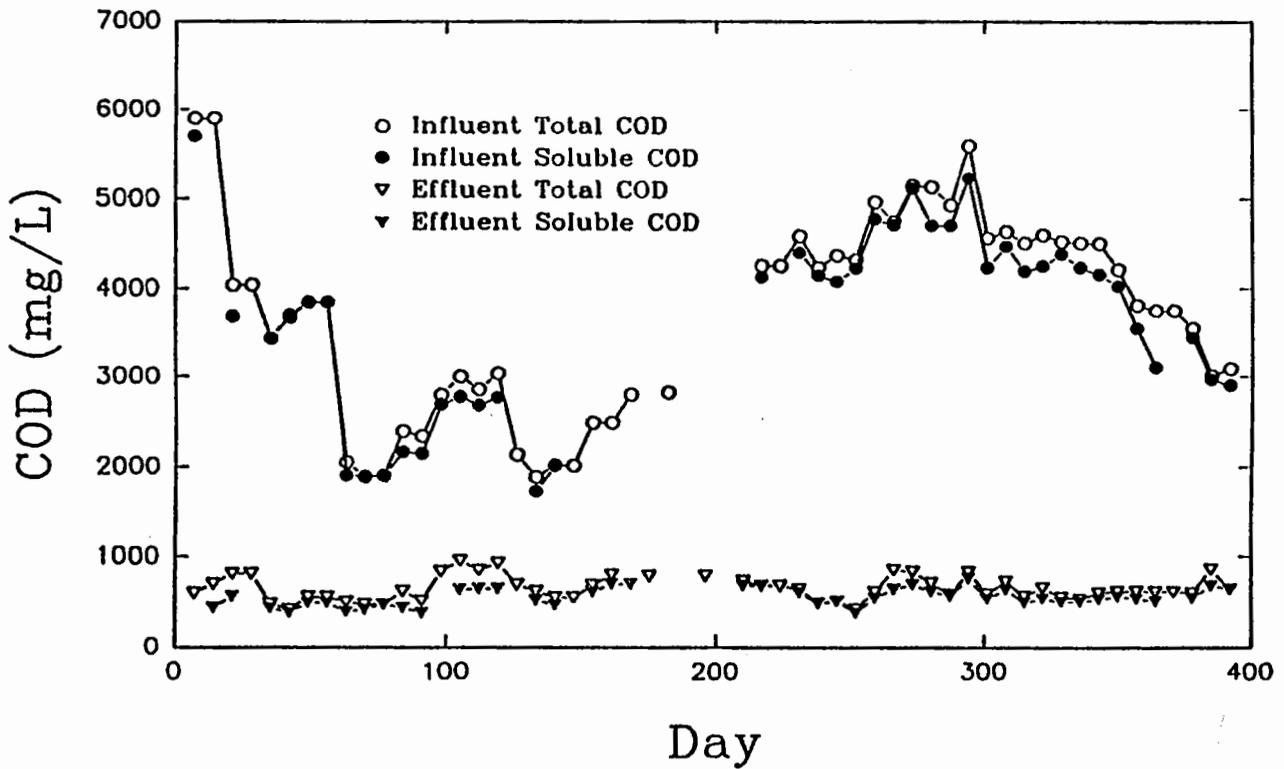


Figure 3: Influent and Effluent COD Concentrations for Reactor B.

Table 3: Reactor A Influent and Effluent Parameters  
During 100% SOC Spiking Phase

Parameter*	Influent A		Effluent A	
Total COD	1,131	(130)#	836	(164)
Soluble COD	1,016	(92)	775	(154)
Acetate	23		14	
Propionate	14		6	
Butyrate	66		51	
Sulfate	89	(41)	21	(17)
Ammonia Nitrogen	306	(99)	304	(97)
Nitrate Nitrogen	0.6	(0.2)	0.5	(0.2)
TSS	159	(35)	195	(60)
VSS	80	(28)	84	(24)
Copper	0.06	(0.08)	0.04	(0.02)
Iron	13.4	(7.1)	9.1	(4.9)
Magnesium	187.4	(40.8)	189.9	(39.2)
Manganese	2.0	(0.5)	1.7	(0.6)
Nickel	0.2	(0.1)	0.2	(0.1)
Lead	0.1	(0.3)	0.1	(0.3)

\* All concentrations in mg/L.

# Standard deviation.

predominant removal mechanism. Tables 5 and 6 summarize SOC removals in Reactors A and B, respectively.

High removal efficiencies were observed for the volatile compounds. The three ketones, acetone, methyl ethyl ketone, and methyl isobutyl ketone (MIK), were efficiently removed in both reactors with removal rates in excess of 95%. In most cases, this would be acceptable for a pretreatment process. In Figure 4, influent and effluent MIK concentrations are plotted as an example from this group.

Of the chlorinated aliphatic compounds, trichloroethylene (TCE) and methylene chloride were consistently reduced to low levels. TCE concentrations decreased 98% in Reactor A and 99% in Reactor B, while methylene chloride concentrations decreased 95% and 96% for Reactors A and B, respectively. One chlorinated aliphatic compound, DCA, required a longer period of microbial acclimation before high removal rates were obtained. In Figure 5, effluent concentrations of DCA are shown to have increased as breakthrough occurred between Days 125 and 250. With a higher concentration of DCA in the bulk liquid, organisms utilizing DCA were able to acclimate to the compound. After a number of weeks at the ultimate (100%) spike feed rate, DCA concentrations began to drop and beyond Day 268 DCA removal averaged 91% in both reactors.

Table 4: Reactor B Influent and Effluent Parameters  
During 100% SOC Spiking Phase

Parameter*	Influent B		Effluent B	
Total COD	3,846	(1,093)#	704	(165)
Soluble COD	3,759	(1,059)	622	(117)
Acetate	1,037		46	
Propionate	467		22	
Butyrate	284		56	
Sulfate	32	(34)	3	(7)
Ammonia Nitrogen	311	(47)	296	(49)
Nitrate Nitrogen	0.9	(0.4)	0.6	(0.2)
TSS	370	(169)	335	(211)
VSS	188	(81)	140	(65)
Copper	0.06	(0.10)	0.02	(0.02)
Iron	55.9	(40.3)	19.7	(11.7)
Magnesium	145.7	(31.7)	139.8	(23.8)
Manganese	3.0	(1.2)	0.6	(0.2)
Nickel	0.1	(0.1)	0.1	(0.1)
Lead	0.1	(0.3)	0.2	(0.5)

\* All concentrations in mg/L.

# Standard deviation.

Table 5: Reactor A Influent and Effluent SOC Concentrations  
During 100% SOC Spiking Phase

Compound*	Influent Average	Effluent Average	Percent Removal
Acetone	10,169 (758)#	189 (216)	98
Methyl Ethyl Ketone	5,027 (282)	70 (68)	99
Methyl Isobutyl Ketone	1,006 (53)	35 (16)	97
Trichloroethylene	397 (20)	8 (10)	98
Methylene Chloride	1,239 (84)	65 (50)	95
1,1-Dichloroethane	101 (5)	20 (17)	80
Chlorobenzene	1,094 (58)	67 (42)	94
Ethylbenzene	607 (34)	34 (19)	94
Toluene	7,960 (410)	436 (303)	95
Phenol	2,628 (171)	22 (23)	99
Nitrobenzene	514 (61)	6 (16)	99
1,2,4-Trichlorobenzene	203 (17)	10 (15)	95
Dibutyl Phthalate	212 (26)	26 (29)	88

\* All concentrations in µg/L.

# Standard deviation.

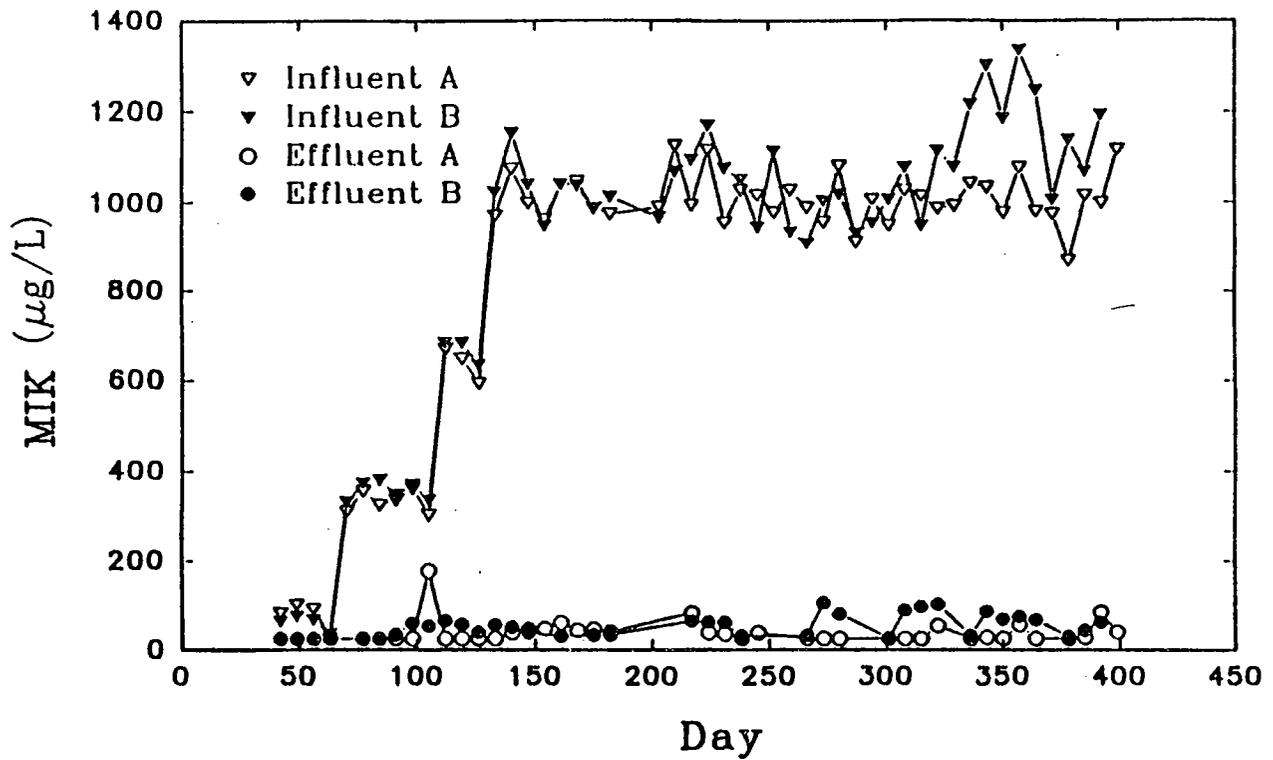


Figure 4: Methyl Isobutyl Ketone Concentrations.

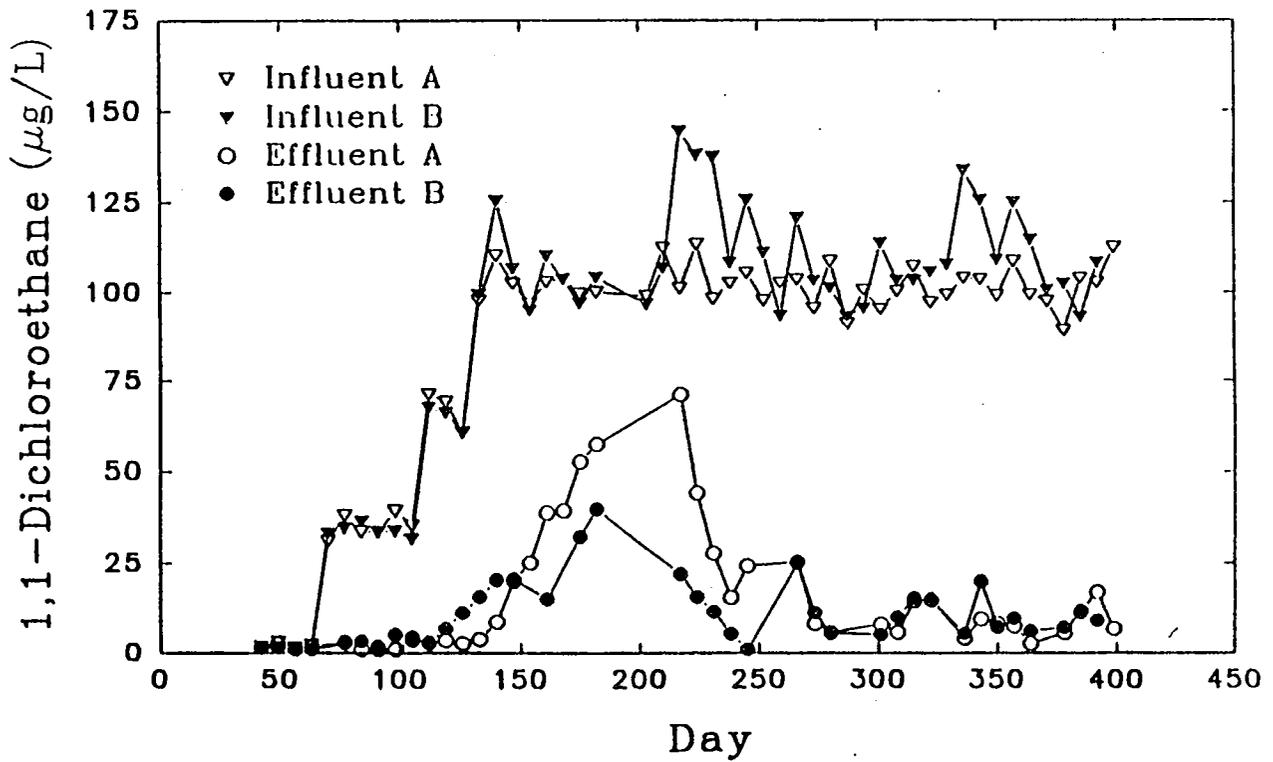


Figure 5: 1,1-Dichloroethane Concentrations.

Table 6: Reactor B Influent and Effluent SOC Concentrations  
During 100% SOC Spiking Phase

Compound*	Influent Average		Effluent Average	Percent Removal
Acetone	12,077	(2,900)#	410 (577)	97
Methyl Ethyl Ketone	9,570	(5,016)	220 (150)	98
Methyl Isobutyl Ketone	1,065	(104)	58 (25)	95
Trichloroethylene	408	(29)	5 (3)	99
Methylene Chloride	1,284	(120)	46 (44)	96
1,1-Dichloroethane	110	(13)	14 (8)	87
Chlorobenzene	1,120	(80)	165 (86)	85
Ethylbenzene	619	(45)	85 (41)	86
Toluene	8,243	(604)	1,102 (744)	87
Phenol	2,929	(504)	93 (63)	97
Nitrobenzene	525	(100)	8 (17)	99
1,2,4-Trichlorobenzene	203	(15)	14 (16)	93
Dibutyl Phthalate	215	(21)	36 (30)	84

\* All concentrations in µg/L.

# Standard deviation.

Removal of aromatic volatile compounds was noticeably greater in the sulfate-reducing conditions of Reactor A than in the methanogen-dominating environment of Reactor B, although removal rates in both were encouraging. Reactor A averaged 94% removal of chlorobenzene and ethylbenzene and 95% removal of toluene. For the same compounds, Reactor B removals averaged 85, 86, and 87%, respectively. For all three compounds, effluent concentrations for Reactor B slowly increased with time initially, but eventually decreased or stabilized. This pattern is similar to that of DCA, where acclimation occurred only when bulk liquid concentrations were sufficient to force acclimation. Influent concentrations of these three compounds were slightly greater for Reactor B because of differences in the two raw leachates. However, the modest differences in influent concentrations do not appear large enough to contribute significantly to the differences in removal efficiencies. Rather, the contrasting reactor environments may be responsible.

For all of the VOCs except chlorobenzene and ethylbenzene, effluent concentrations from Reactor A did not change significantly after GAC replacement was halted. This indicates that compounds were degraded in the reactor and that GAC replacement did not control the high removal efficiencies. Although chlorobenzene and ethylbenzene effluent concentrations were slightly higher with no GAC replacement, they were still adequate for most situations.

Off gases from Reactors A and B were analyzed for VOCs to investigate the importance of stripping losses. In Reactor A, none of the VOCs were seen in significant amounts in the off gas, further indicating that biological activity was responsible for SOC removal. With the substantial amount of gas produced in Reactor B (14 L/day during gas sampling periods), a higher potential for VOC

stripping was present. Ethylbenzene and toluene were lost in Reactor B off gases at average rates equal to 18% and 11% of the influent loading rates, respectively. These were two of the compounds with the lowest overall removal rates in Reactor B.

Most of the semivolatile compounds were effectively removed from both leachates. Because of analytical problems, results for bis (2-ethylhexyl) phthalate are inconclusive regarding the fate of the compound and are not included in Tables 5 and 6.. Phenol removal rates remained nearly constant at 99% for Reactor A and 97% for Reactor B (Figure 6). Likewise, nitrobenzene was essentially nonexistent in the effluents, with both reactors achieving 99% removal of the compound. Reactor A achieved 95% removal of trichlorobenzene, while 93% was removed in Reactor B. Dibutyl phthalate removal rates were adequate but not outstanding, averaging 88% in Reactor A and 84% in Reactor B.

### CONCLUSIONS

Because of variations in raw leachate characteristics, two different anaerobic environments were encountered in the expanded-bed reactors. One reactor receiving a feed stream with a low biodegradable COD level exhibited a symbiotic competition between sulfate-reducing bacteria and methanogens, while the second reactor receiving a high biodegradable COD feed operated strictly as a methanogenic unit. Both reactors achieved acceptable SOC removal rates for a pretreatment process.

A comparison of the two systems indicates that a sulfate-reducing environment may produce equal or better performance than a methanogenic environment in removing a consortium of hazardous chemicals from waste streams. All three volatile aromatic compounds in the SOC consortium were removed at higher rates in the sulfate-reducing environment.

Effluent COD concentrations from both reactors were sufficiently low that discharges of the pretreated leachates would not overload aerobic wastewater treatment systems. Both systems responded well to seasonal variations in leachate strength, indicating the adaptability of the anaerobic GAC expanded-bed reactor.

### ACKNOWLEDGMENTS

Funding for this work was provided by U.S. EPA under Contract Nos. 68-03-4038 and 68-C9-0036. The authors wish to thank Dolloff F. Bishop, the technical support staff at the U.S. EPA Risk Reduction Engineering Laboratory, personnel at the U.S. EPA Test and Evaluation Facility, and personnel at the Delaware Solid Waste Authority.

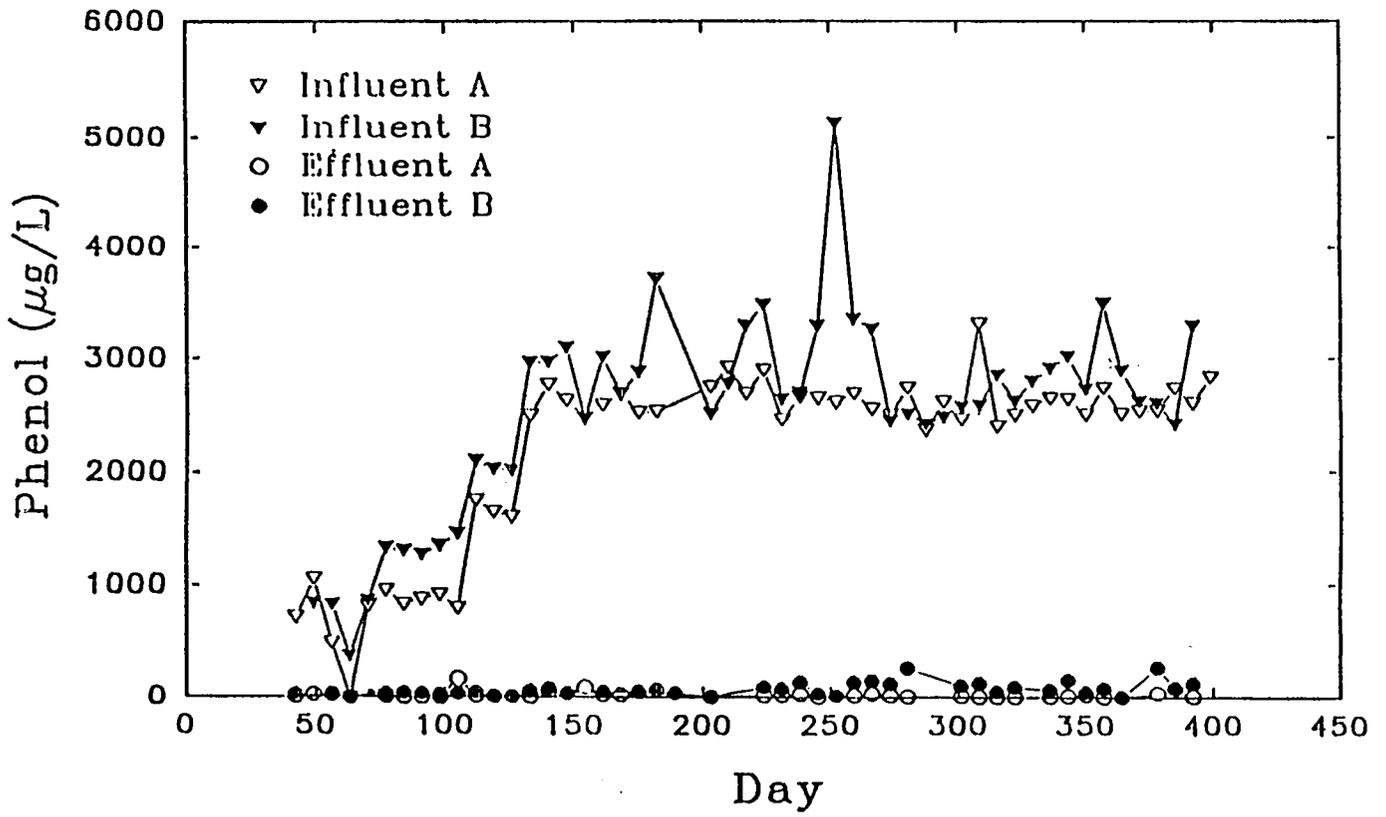


Figure 6: Phenol Concentrations.

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ANAEROBIC PRETREATMENT OF AN INDUSTRIAL WASTE CONTAINING SEVERAL VOC'S

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ABSTRACT

The effectiveness of an anaerobic granular activated carbon (GAC) expanded-bed bioreactor was evaluated relative to the pretreatment of high strength industrial wastes containing RCRA volatile organic compounds (VOC's). A total of six VOC's, methylene chloride, chlorobenzene, carbon tetrachloride, chloroform, toluene, and tetrachloroethylene, were fed to the reactor in a high strength matrix of background organic compounds. Operation of the reactor resulted in excellent removals of all VOC's (> 97%). Chloroform, while itself removed at levels in excess of 97%, was found to inhibit the degradation of acetate and acetone, two of the base organic compounds. Without any source of chloroform in the feed (either chloroform or its precursor carbon tetrachloride), excellent COD removals were obtained in addition to near-complete removal of all the other VOC's.

KEY WORDS: Granular activated carbon (GAC); anaerobic processes; expanded-bed; volatile organic compound (VOC); chloroform; carbon tetrachloride; chlorobenzene; methylene chloride; tetrachloroethylene (PCE); trichlorethylene (TCE); vinyl chloride; toluene.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

## INTRODUCTION

Many volatile organic compounds (VOC's) are known or suspected carcinogens. They are extensively used in industry as degreasing and cleaning fluids, refrigerants, and solvents. As such, they are often present in appreciable concentrations in industrial wastewaters and their fate in treatment systems is an issue of significant concern. Conventional aerobic processes are often unable to satisfactorily detoxify VOC's due to the extreme volatility of these compounds and because the high aeration rates commonly used in aerobic biological processes result in excessive stripping into the gas phase<sup>1</sup>. Furthermore, while non-chlorinated VOC's seem to be readily biodegraded aerobically<sup>2</sup>, chlorinated VOC's for the most part resist aerobic breakdown and stripping tends to be the dominant mechanism for their removal<sup>1,2</sup>.

Anaerobic treatment offers two distinct advantages for the treatment of VOC's: first, the effect of stripping is substantially diminished compared to that in aerobic processes. Stripping in an anaerobic process could occur only due to the production of methane gas, and, typically, the amount of gas produced is significantly smaller than the normal aeration rates employed in aerobic processes. For example, 1 kg of COD fed to an anaerobic reactor would produce about 395 L of methane under mesophilic conditions, which, assuming a gas composition of 60% methane and an appropriate moisture content, would translate to a gas production of 697 L. To treat the same 1 kg of COD aerobically, typically, 0.7 kg of O<sub>2</sub> would be required<sup>3</sup>, which, assuming an air composition of 23.2% by weight of O<sub>2</sub>, an oxygen transfer efficiency of 10%, and an operating temperature of 20°C, yields an aeration flow rate of about 25,000 L. This is approximately 38 times the gas production rate in the anaerobic treatment process treating the same strength COD. Thus, stripping of VOC's will occur to a much greater extent when wastewater is treated aerobically than when it is treated anaerobically.

The second distinct advantage of anaerobic treatment of VOC's over aerobic treatment is that biodegradation of chlorinated compounds under anaerobic conditions occurs by reductive dehalogenation, and, as such, the greater the number of chlorine atoms on a compound the more easily it will be anaerobically degraded. Several recent studies have shown that many of the VOC's appearing on the Resource Conservation and Recovery Act (RCRA) list of compounds are amenable to biodegradation under anaerobic conditions. Tetrachloroethylene (PCE), for example, has been shown to be biotransformed by reductive dehalogenation to trichloroethylene (TCE), dichloroethylene (DCE), and vinyl chloride in a continuous-flow fixed film column<sup>4</sup>. Similar tests under aerobic conditions exhibited no biotransformation of PCE<sup>5</sup>. Carbon tetrachloride has been shown to be biologically transformed to chloroform and methylene chloride in the presence of *Clostridium sp.*, a strictly anaerobic bacterium<sup>6</sup>. Chloroform biodegrades under anaerobic conditions; however, higher concentrations have been shown to inhibit the cultures<sup>7,8</sup>. Removal of chloroform by aerobic methods has proven unsuccessful<sup>9</sup>. Methylene chloride, on the other hand, has been demonstrated to readily degrade both anaerobically<sup>10</sup> and aerobically<sup>11,12,13</sup>. Chlorobenzene and other chlorinated benzenes have been shown to degrade aerobically but not anaerobically<sup>5</sup>. Toluene has been shown to degrade under both aerobic<sup>14,15,16</sup> and anaerobic conditions<sup>17</sup>. Thus, anaerobic treatment appears

to be a promising technology for the detoxification of many chlorinated VOC's.

When treating high strength industrial wastewaters, the toxicity of the compounds involved is also a major concern as inhibitory concentrations or accidental discharges of toxic compounds in a waste stream can completely destroy a microbial community. There is, therefore, considerable merit in combining carbon adsorption with anaerobic biological treatment while treating high strength industrial wastes. Such a combination should effect efficient removal of toxic substances via adsorption as well as biological degradation of VOC's, many of which are biodegradable only under anaerobic conditions. Also associated with such a system would be the cost-saving advantages of anaerobic treatment resulting mainly from the conversion of organic chemical oxygen demand (COD) to valuable methane gas with minimal sludge production.

Investigations of the anaerobic granular activated carbon (GAC) expanded-bed bioreactor have demonstrated the effectiveness of the technology in treating high strength industrial wastewaters. Suidan *et al.*<sup>18,19</sup> and Khan *et al.*<sup>20,21</sup> showed the effectiveness and resiliency of the process in treating synthetically prepared phenol and catechol solutions. In subsequent studies, this process was used to treat a mixture of biodegradable and biologically resistant and toxic polycyclic nitrogen compounds<sup>22</sup>. The anaerobic GAC reactor has also been used for the treatment of coal gasification wastewaters<sup>23-27</sup> and for the treatment of high strength industrial wastes containing chlorinated organic solvents<sup>28</sup>. COD removal efficiencies of over 90% were consistently obtained in these studies for COD volumetric loading rates that sometimes exceeded 28 kg/m<sup>3</sup>\*d<sup>27</sup>.

This study was designed to assess the potential of the anaerobic GAC expanded-bed bioreactor in treating VOC's present in high strength industrial wastewaters. A simulated wastewater consisting of several RCRA VOC's in a base flow of non-RCRA organic compounds served as the system feed. The unit was designed as a pretreatment system with emphasis on treatment of the VOC's and not on the reduction of COD, which was contributed almost entirely by the non-RCRA organic compounds.

## MATERIALS AND METHODS

### EXPERIMENTAL APPARATUS

The reactor system consisted of a jacketed column, recycle system, feed system, and gas collection system. The anaerobic chamber (10.2-cm ID)(Figure 1) had a volume of 11 L and was maintained at 35°C. An internal recycle stream at a recycle rate of 5 L/min provided an initial bed expansion of 25% and helped maintain a completely-mixed regime in the reactor. The reactor was charged with 1.5 kg of 16x20 U.S. mesh F400 GAC (Calgon Carbon Corp.) resulting in an unexpanded bed height of 43.2 cm and an apparent density of 0.43 g/cm<sup>3</sup>.

A gas collection system was devised to collect the gas, measure its production rate, and then vent it to a hood. A wet tip gas meter was used to measure the gas production rate. The system feed was prepared as three separate solutions consisting of an organic feed, a buffer solution, and a nutrient

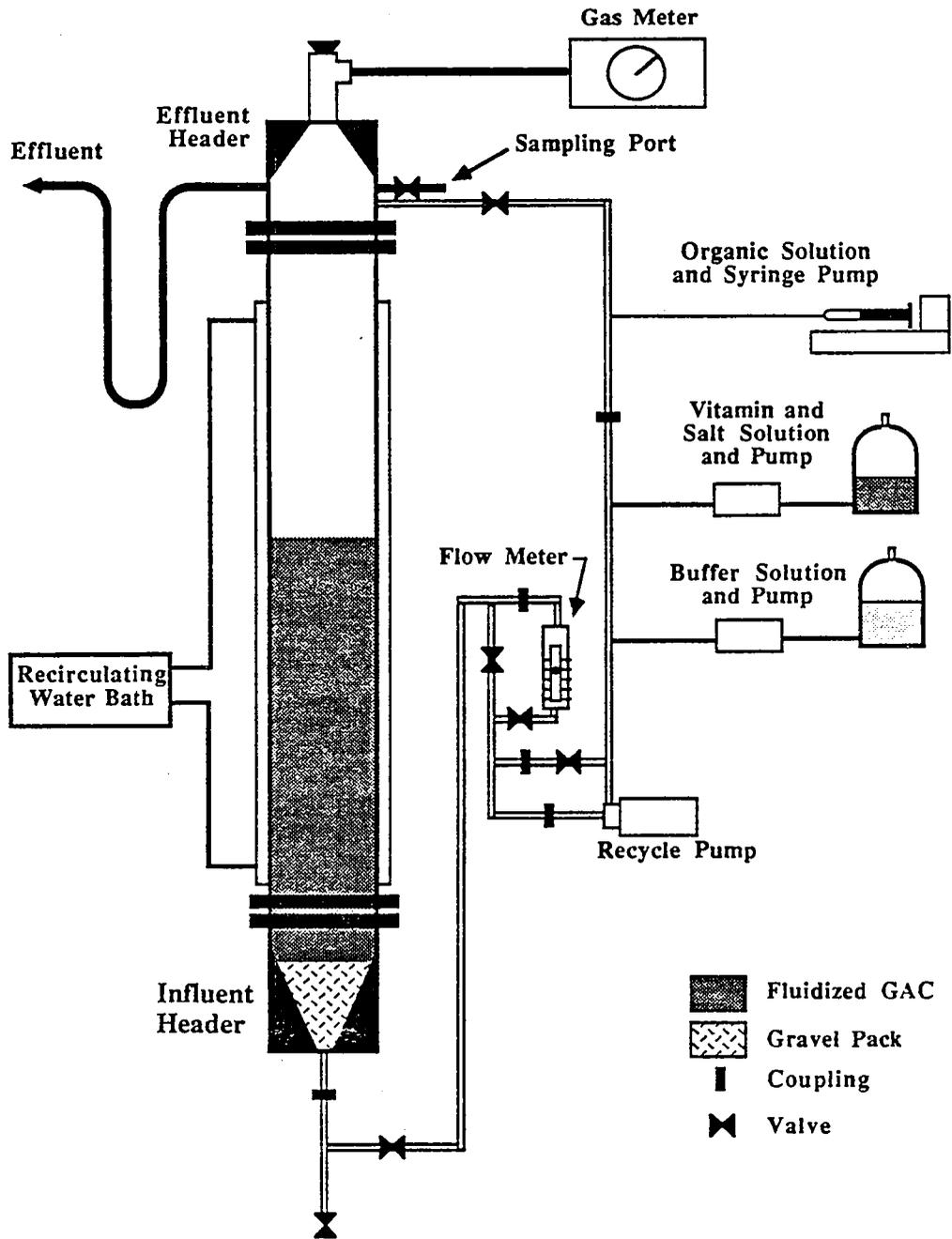


Figure 1. Schematic of Anaerobic Expanded-Bed Treatment System

solution. The organics, buffer solution, and nutrient solution were all fed directly into the suction side of the column recycle loop to thoroughly mix the contents prior to entry to the reactor. The VOC's were fed to the reactor from a 25-mL syringe connected to a variable-speed syringe pump. The speed of the pump was adjusted to run continuously over a 24-hour period. The pump syringe was refilled on a daily basis by connecting another syringe with new organic feed to a three-way valve near the tip of the pump syringe. The pump syringe was connected to the column using stainless steel tubing.

The buffer and nutrient solutions were fed to the reactor from separate 55-L plastic reservoirs, calibrated at 1-L divisions. The solutions were pumped with separate fixed-speed positive displacement pumps connected to separate timers. Tygon tubing was used to feed the solutions to the reactor.

#### SYNTHETIC INDUSTRIAL WASTEWATER AND NUTRIENTS

The target influent concentrations of the organic feed constituents are given in Table 1. Acetone, methanol, and acetic acid represent the background organic compounds typically found in industrial wastes. Due to the volatility of the solvents and organics, the organic feed to the reactor was prepared every 2 to 4 weeks and stored in 25-mL amber septum vials with a PTFE-faced septum at 4°C. The total daily volume of the three background organic compounds with the RCRA VOC's was greater than the volume of the syringe (25 mL). Attempts to use a larger syringe (50 mL), however, resulted in pump failure. To reduce the volume to below 25 mL, acetic acid was taken out of the organic feed and added to the buffer solution.

Table 1. Target Composition of Synthetic Industrial Wastewater  
(All concentrations in mg/L)

<u>Parameter</u>	<u>Concentration</u>
<u>Volatile RCRA Compounds</u>	
Carbon Tetrachloride	20
Chlorobenzene	20
Chloroform	20
Methylene Chloride	20
Tetrachloroethylene	20
Toluene	20
<u>Background Organic Compounds</u>	
Acetic acid	1565
Methanol	1110
Acetone	755

The buffer solution containing sodium carbonate (6000 mg/L) was added to maintain a near neutral pH. Ammonium carbonate (775 mg/L) and sodium sulfide (300 mg/L) were added to the buffer solution as nutrients. Acetic acid at a

concentration of 3130 mg/L was also added to the buffer solution. The buffer solution was fed into the system at a flow rate of 4 L/day, which represented 49.9% of the system influent flow.

To supply the necessary micronutrients required for the growth of microorganisms, a solution containing inorganic nutrients and vitamins was fed to the reactor. The flow rate was identical to that of the buffer solution (4 L/day). Stock salt and vitamin solutions were made periodically and stored at 4°C until needed. The composition of the nutrient solution is given elsewhere<sup>29</sup>.

## ANALYTICAL METHODS

Daily measurements were taken of the volume of gas produced and the flow rates of the buffer, nutrient, and organic stock solutions. Room temperature, pH, and water bath temperature were also monitored daily. Effluent samples were analyzed for VOC's on a weekly basis. Analyses for acetate, COD, and gas composition were also performed weekly.

Four of the six RCRA VOC's, methylene chloride, chloroform, carbon tetrachloride, and tetrachloroethylene (PCE), were analyzed using a purge and trap (Model 14-000-40, Tekmar Co.) followed by electron capture detection on a gas chromatograph (GC) (Model 5980, Hewlett Packard). A megabore capillary column (J&W Scientific, DB-624) was used for separation. The purge and trap was run with a 15-minute purge at room temperature, which included a 4-minute dry purge, followed by a 4-minute desorb at 180°C, and finally a 7-minute bake at 225°C. The GC was programmed from 35°C to 90°C at 5°C/minute with a 5-minute hold at 35°C, then from 90°C to 150°C at 30°C/minute with a 4-minute hold at 150°C. The carrier gas for the purge and trap and the GC was ultra-high purity helium. The purge flow rate was 40 mL/minute, and the carrier flow rate was 8 mL/minute. P-5, used as a make-up gas, was applied at a flow rate of 50 mL/minute. Injector and detector temperatures were 120°C and 260°C, respectively.

Sample injection volume for aqueous samples of these four compounds was 5 mL using a glass hypodermic syringe with a Luer-Lok tip. Water used for blanks and dilutions was prepared by purging nitrogen gas through distilled water for at least 10 minutes. Standards were prepared following EPA Method 502.2, Section 6.3.1. At least four different standard concentrations were analyzed, with one standard containing concentrations slightly higher than its detection limits and the rest in the linear output range.

Effluent samples were filtered using a 10-mL syringe with an attached 0.45- $\mu$ m membrane filter. This filtration step was found to cause no detectable losses of the VOC's. Samples were analyzed within 2 hours of being taken. If samples could not be analyzed immediately, the samples were acidified (pH < 2.0) and stored without headspace in 40-mL amber septum vials with PTFE-faced silicone septum at 4°C. The release of carbon dioxide as a result of acidification was found to cause no VOC losses. Stored samples were analyzed within 1 week.

To determine what fraction, if any, of the different VOC's was being

stripped into the gas phase, the product gas was sampled and analyzed by direct injection into the purge and trap. The gas sample was obtained directly from a septum placed in the product gas line. The volume of the gas sample to be used was adjusted to maintain a response within the linear output range of the compounds on the chromatogram. For the analysis of the gas from this reactor, a sample size of 1 mL ensured that all the compound peaks were in the linear range. The gas phase concentrations thus determined were used in conjunction with the daily gas flow rate to determine the total mass of each of the VOC's being stripped daily. These were then compared with the daily influent and effluent mass flow rates of the VOC's to provide a better assessment of the fate of the various compounds.

Because a PID/Hall detector was not available at the time of the study, analysis for two of the VOC's, toluene and chlorobenzene, was performed using a Hewlett Packard 5890A GC and a flame ionization detector (FID). A DB-5 megabore column (J&W Scientific) was used for separation of the compounds. Ultra high purity helium, at a flow rate of 15 mL/min, was used as the carrier gas. Hydrogen and air at flow rates of 30 mL/min and 400 mL/min, respectively, were used to fuel the flame.

Preparation of this sample for injection involved two steps. First, a 250-mL sample was acidified (to a  $\text{pH} < 2$ ) and passed through a packed bed of XAD-2 resin at a flow rate not exceeding 10-15 mL/min. The compounds were subsequently extracted off the XAD-2 resin using methylene chloride. A known mass (0.1 mg) of the internal standard, 2,4,6-trichlorophenol (TCP), was added at this stage (100  $\mu\text{L}$  of 1 g/L stock TCP) prior to injection into the gas chromatograph.

Standard curves were prepared for three different concentrations of each compound. The standards used in preparing these curves were processed in exactly the same manner as were the reactor effluent samples. The mass ratios of the compounds to the internal standard were plotted versus the ratio of the areas of the compound peak and the internal standard. Using these standard curves, the area ratio obtained from the injection of the sample was used to determine the mass ratio of the compound to the internal standard. Since the mass of the internal standard in the injection sample was known, the mass of the compound could be calculated. From the initial volume of sample passed through the resin, the concentration of the compound was obtained. The efficiencies of extraction of the VOC's were determined by comparing the chromatograms from standards that were prepared directly in methylene chloride to aqueous samples that had been extracted on the resin. The extraction efficiency for toluene was 50%, while that for chlorobenzene was 49%.

Amberlite XAD-2 resin was used for the extraction process. The resin was cleaned thoroughly prior to use by the following procedure. Eighty grams of resin were washed with a 2% ammonium carbonate solution for 20 minutes. The resin was then rinsed with 500 mL of distilled water. Sequential extraction in a soxhlet apparatus using water, methanol, and diethyl ether for 24 hours in each solvent followed. The volume of each solvent was 300 mL. At the end of the ether reflux, the resin was rinsed successively with 200 mL of methanol and 1000 mL of distilled water. The aqueous slurry of resin was stored in methanol in glass stoppered bottles until use.

Acetic acid was measured by gas chromatography using a Hewlett Packard 5710A GC equipped with an FID detector. Samples were diluted, if necessary, in 1% formic acid dilution water. The analysis was done at a constant oven temperature of 100°C using a 60/80 Carbopack, C/0.3% Carbowax 20M/0.1% H<sub>3</sub>PO<sub>4</sub> glass column. The carrier gas was nitrogen applied at a flow rate of 30 mL/min. The injection temperature was 180°C, and the detector temperature was 250°C.

Product gas was sampled weekly through a septum in the gas line. The gas samples were analyzed for methane, nitrogen, carbon dioxide, and oxygen as percentages of the total gas volume. A gas partitioner and certified gas standards were used for the gas analysis.

COD was measured using a Hach COD Reactor (Model 16500-10) with prepared digestion vials.

## EXPERIMENTAL RESULTS AND DISCUSSION

### REACTOR OPERATION

Prior to the addition of the VOC's, the reactor was gradually acclimated to the background organic compounds fed at the desired COD loadings over a 4-month period. Day 1 corresponds to the time when steady-state conditions were achieved in the reactor. Steady-state operating conditions were maintained for approximately 2 weeks, Day 1 to Day 15, prior to the addition of the VOC's. The total flow to the system during this period was 8.02 L/day, consisting of 4 L/day vitamin and nutrient solution, 4 L/day buffer solution containing acetic acid, and about 20 mL/day of the remaining two background organic compounds. The three background organic compounds were added in equal COD proportions totalling 5000 mg/L. Gas production during the steady-state background period averaged 18 L/day, and the filtered effluent COD was approximately 100 mg/L. Both these numbers correspond to COD removal efficiencies of greater than 90%. No partial replacement of the carbon medium with virgin GAC was practiced during this period.

The RCRA VOC's were added to the background feed on Day 16 at 25% of the target strength listed in Table 1 (5 mg/L). Carbon replacement at 15 g/day, or 1% of the total carbon bed, was initiated on Day 25. Table 2 lists the subsequent changes in both VOC influent concentrations and carbon replacement rates. As is the case with any methanogenic reactor, gas production and effluent COD were taken to be good indicators of reactor performance. These parameters were monitored closely for indications of inhibitory effects of the VOC's. No such effects were observed, and the daily gas production rate and weekly filtered effluent COD remained stable at 18 L/day and 180 mg/L, respectively. Effluent VOC concentrations were not analyzed until Day 123 due to delays associated with analytical method development.

Table 2. Date of VOC Concentration or GAC Replacement Rate Variations

Date	Day	Carbon Tetrachloride conc. (mg/L)	Chloroform conc. (mg/L)	Remaining VOC Conc. (mg/L)	GAC Replacement (g/day)
1/1/89	0	0	0	0	0
1/16/89	16	<u>5</u> *	<u>5</u>	<u>5</u>	0
1/25/89	25	5	5	5	<u>15</u>
3/18/89	77	<u>10</u>	<u>10</u>	<u>10</u>	15
4/30/89	120	<u>20</u>	<u>20</u>	<u>20</u>	15
5/30/89	150	20	<u>10</u>	20	15
9/15/89	164	20	10	20	<u>30</u>
6/30/89	181	20	<u>0</u>	20	30
7/26/89	207	20	0	20	<u>15</u>
8/17/89	229	20	0	20	<u>0</u>
2/15/90	411	<u>0</u>	0	20	0

\* Bold type with underline indicates the change made to the operating conditions. Plain type indicates a continuation of the current operating conditions.

Consequently, on Day 77, the influent concentration of each of the VOC's was doubled to 10 mg/L while maintaining a constant 15-g/day carbon replacement rate. Stable operating conditions were observed; however, the daily gas production rates were higher than those of the previous phase at around 20 L/day and filtered effluent COD values were slightly lower at about 70 mg/L. This gas production rate represents a conversion of 102% of the theoretically attainable gas production if all the influent COD were converted to methane. A possible explanation for the higher gas production rate is an increase in biomass within the reactor that lead to the utilization of previously adsorbed compounds.

Since no inhibitory effects were observed by Day 120, the influent concentration of all the VOC's was again doubled to 20 mg/L. Weekly analysis of effluent VOC concentrations was begun on Day 123 and continued throughout the rest of the study.

Figure 2 presents the influent and effluent COD and the COD equivalent of the methane gas produced versus time. On approximately Day 140, the daily gas production exhibited a steady decrease from approximately 19 L/day to a new plateau of 13 L/day over a time period of 1 week. Accompanying the decrease in gas production was a corresponding increase in effluent COD values. The filtered effluent COD concentration increased from 145 mg/L on Day 129 to 1370 mg/L by Day 147. The effluent concentrations of all VOC's remained low and stable, except for chloroform, which showed a sharp increase from 65  $\mu\text{g/L}$  on Day 141 to 102  $\mu\text{g/L}$  on Day 150. Chloroform was, therefore, believed to be the primary cause of inhibition.

Figure 3 shows the concentration of influent and effluent chloroform and effluent COD versus time from Day 123 onward. As can be seen, there is a definite relationship between the effluent COD and effluent chloroform concentrations, further confirming the hypothesis that chloroform was indeed the cause of inhibition. Two strategies were attempted to return the system to previous operating conditions. First, the influent concentration of chloroform was decreased to 10 mg/L on Day 150, leaving the other VOC's at 20 mg/L. Lowering the influent chloroform concentration did not alleviate the inhibition and, subsequent GC analysis showed no decrease in effluent chloroform concentrations. Rather, the effluent chloroform concentration increased further to 265  $\mu\text{g/L}$  by Day 163, while effluent COD remained above 1000 mg/L and daily gas production remained at 13 L/day.

An attempt was also made to determine whether carbon adsorption could suppress the inhibitory effects of chloroform. The carbon replacement rate was doubled to 30 g/day on Day 164. Prior to initiating the new replacement rate, 175 grams of carbon was removed from the column and replaced with 100 grams of virgin carbon and 75 grams of biological carbon from a similar column treating acetate and phenol. The batch carbon replacement and the new replacement rate did not suppress the effluent chloroform concentration; rather, it continued to gradually increase to a value of 308  $\mu\text{g/L}$  on Day 180. Effluent COD also did not decrease; rather, values increased to 1580 mg/L. It is believed that replacement rates greater than 30 g/day (50-day solids retention time (SRT)) would not be able to control chloroform inhibition any better because chloroform is such a weakly adsorbing compound. Also, higher replacement rates decrease the SRT and may adversely affect the biological removal capabilities of the system.

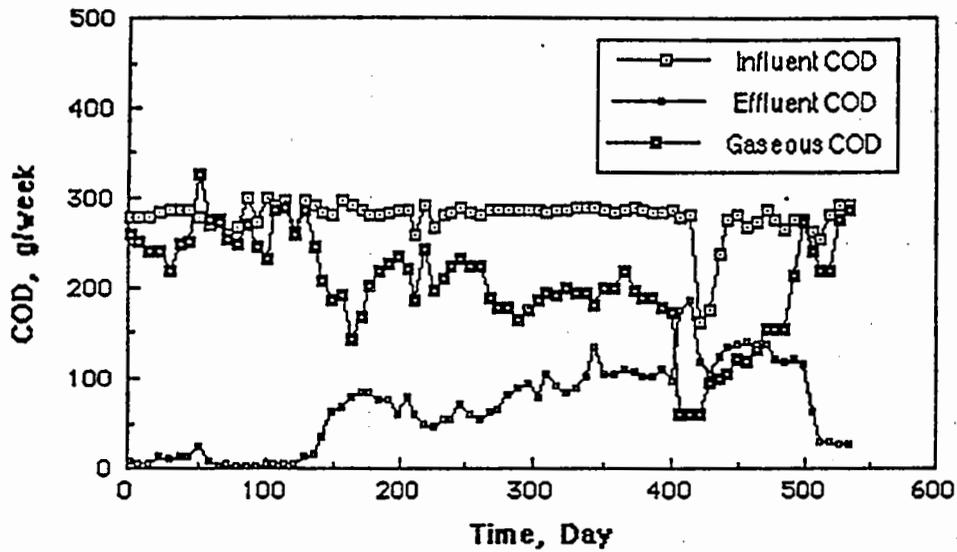


Figure 2. Influent, Liquid Effluent, and Gaseous COD Variations

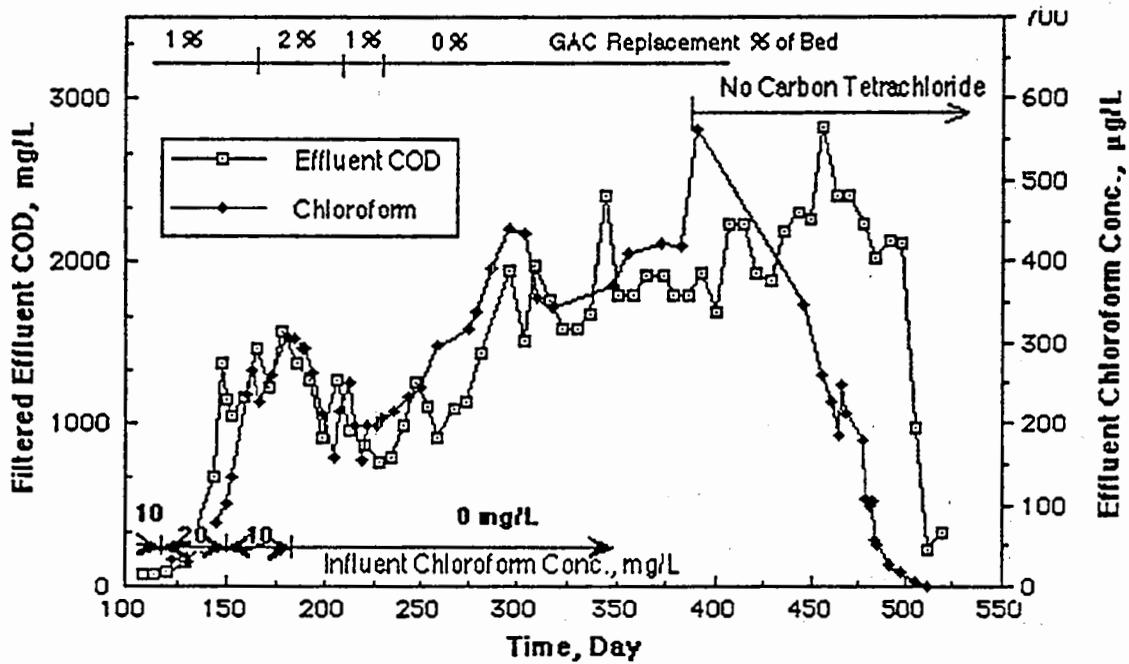


Figure 3. Filtered Effluent COD and Effluent Chloroform Concentration vs. Time

As a result of these upward trends of effluent COD and chloroform concentrations, chloroform was completely removed from the influent on Day 181 while the remaining VOC's were kept at 20 mg/L. Though the effluent chloroform concentration dropped, a significant amount still appeared in the effluent, leading to the conclusion that there was another source of chloroform. Previous studies (5) have shown that carbon tetrachloride is anaerobically degraded to chloroform. Therefore, it was concluded that the chloroform seen in the reactor effluent after removal of chloroform from the feed was a product of carbon tetrachloride degradation.

Accompanying the decrease in chloroform concentration, gas production gradually increased from 13 L/day to a new plateau of 16 L/day. Effluent COD values corresponding to this new plateau were approximately 1000 mg/L. Carbon replacement was maintained at 30 g/day during this recovery period. On Day 207, the carbon replacement rate was returned to 15 g/day. Effluent chloroform concentrations remained stable at approximately 180  $\mu\text{g/L}$ .

On Day 229, it was decided to discontinue carbon replacement completely to allow the system to reach an equilibrium chloroform concentration. Effluent chloroform concentration increased from approximately 200  $\mu\text{g/L}$  to a maximum value of 441  $\mu\text{g/L}$  on Day 296. Subsequently, the concentration dropped, suggesting a trend towards a steady-state operating condition. At this stage, PCE was the only other volatile compound being detected in the reactor effluent. An additional compound, identified to be trichloroethylene (TCE), started appearing in the effluent from approximately Day 200 onward. PCE has been shown in the literature to degrade to TCE and further to dichloroethylene and vinyl chloride. On Day 306, chloride analyses were begun in an effort to quantify the biodegradation of the chlorinated VOC's. A significant increase in chloride production was noted, indicating transformation of the VOC's within the reactor. Around Day 348, the concentration of chloroform in the effluent began rising rapidly. TCE and PCE concentrations also increased, though at a much slower rate. These changes were accompanied by the appearance of methylene chloride and carbon tetrachloride in the effluent. A new compound, identified to be vinyl chloride, also started appearing in the effluent. Quantification of vinyl chloride concentrations began on Day 348.

On Day 411, due to a power failure lasting 12 hours, reactor operation was seriously disturbed. Gas production dropped drastically from 11 L/day to 1 L/day. The feed to the reactor was stopped for 1 day, and 200 g of GAC were added to the reactor. Carbon tetrachloride was completely removed from the feed, and the feed was restarted at 25% of the original rate. Gas production was monitored carefully, and the feed rate was slowly brought back to its original value. The effluent chloroform concentration, which was at 562  $\mu\text{g/L}$  before the accident, decreased rapidly once carbon tetrachloride was removed from the feed. The effluent TCE concentration also increased, with a corresponding decrease in the PCE concentration. The effluent chloroform concentration eventually dropped below detection levels, and gas production increased to a new level of 20 L/day. A rapid decrease in the effluent PCE concentration to levels below the detection limit, with an accompanying increase in the effluent TCE concentration, was also observed in this phase. It is suggested that the sudden increase in gas production following the complete disappearance of chloroform from the effluent had the effect of shearing off the

species responsible for the biotransformation of TCE. This theory of loss of biomass from the reactor was borne out by a visual examination of the effluent and by a comparison of the total and filtered effluent COD values. Subsequently, the TCE concentration in the effluent levelled off at 350  $\mu\text{g/L}$ .

#### DEGRADATION OF BACKGROUND ORGANIC COMPOUNDS

Each of the background organic compounds, acetate, acetone, and methanol, contributes 32.57% of the influent COD with the remaining 2.29% attributable to the RCRA VOC's. Therefore, COD removal across the reactor is a good indicator of the extent of degradation of these compounds. The cumulative COD balance is presented in Figure 4. The total COD out includes the COD of the liquid effluent and the COD equivalent of the methane gas produced. At any time, the difference between these two lines represents the accumulation of COD that was either adsorbed onto the GAC surface (including the COD associated with any GAC that was removed from the reactor) or present in the form of attached biomass.

The slope of the influent COD line at any point represents the rate of COD addition to the reactor, and the slope of the effluent COD line at any point represents the rate at which COD is leaving the reactor. The COD leaving the reactor represents the sum of the effluent aqueous COD and the COD equivalent of the methane gas produced. Only during periods of bioregeneration will the rate of COD release exceed the rate of COD addition. In a non-adsorbing system, the rate of COD release cannot exceed the rate of addition except in cases where sloughing of retained solids occurs. During stable operating periods, the rate of COD addition will only slightly exceed the rate of release.

The total mass of COD retained in the reactor is presented in Figure 5. Since the mass of carbon was kept constant, this figure also represents the loading on the activated carbon. The slope represents the rate of COD adsorption on the carbon. A negative slope indicates that bioregeneration is occurring. As is clearly seen, the reactor experienced frequent periods of bioregeneration, indicating an extremely dynamic system with a transition of quasi steady-state conditions.

The cumulative mass balance in Figure 4 demonstrates good accountability of the COD, even after inhibition began. The average difference between the total COD in and the total COD out was 183 g/1500-g GAC, or 122 mg COD/g GAC. During the phase of zero carbon replacement, 74.5% of the COD removal occurred biologically. Adsorbed compounds and biomass accounted for 0.8% removal for a total removal efficiency of 75.3%, leaving 24.7 % of the COD in the effluent.

Biological degradation of the background organic compounds was measured by the amount of methane and carbon dioxide gas produced. The total loading rate of these compounds was high enough (5000 mg/L as COD) that fluctuations in daily gas production would give an indication of the degree of biological inhibition. Theoretical and actual methane production with time are shown in Figure 6. Chloroform inhibited the degradation of acetate and acetone, two of the background organic compounds, following the increase in chloroform feed rate to 20 mg/L. Hence, during the inhibitory phase, methane production was well below the theoretically predicted rate. After the complete removal of all

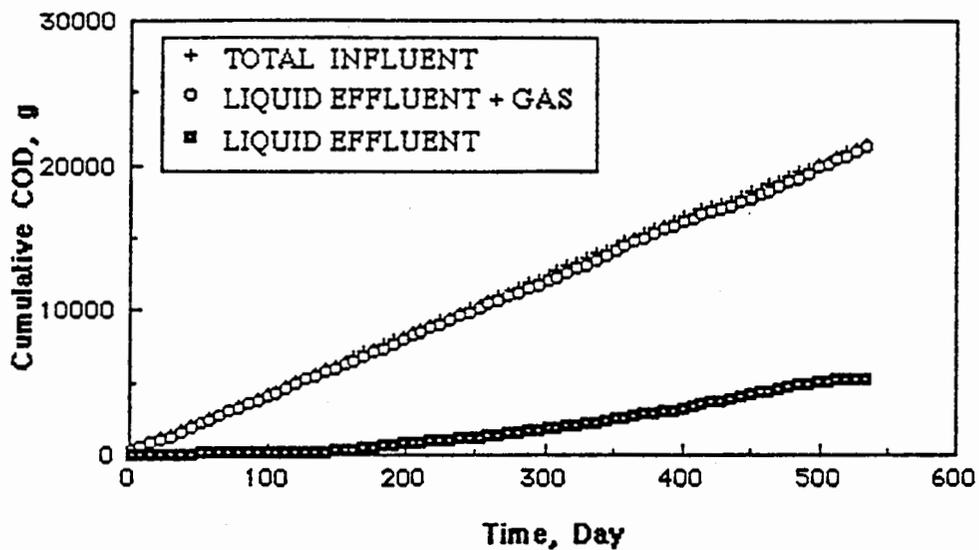


Figure 4. Cumulative Total Influent, Total Effluent, and Liquid Effluent COD

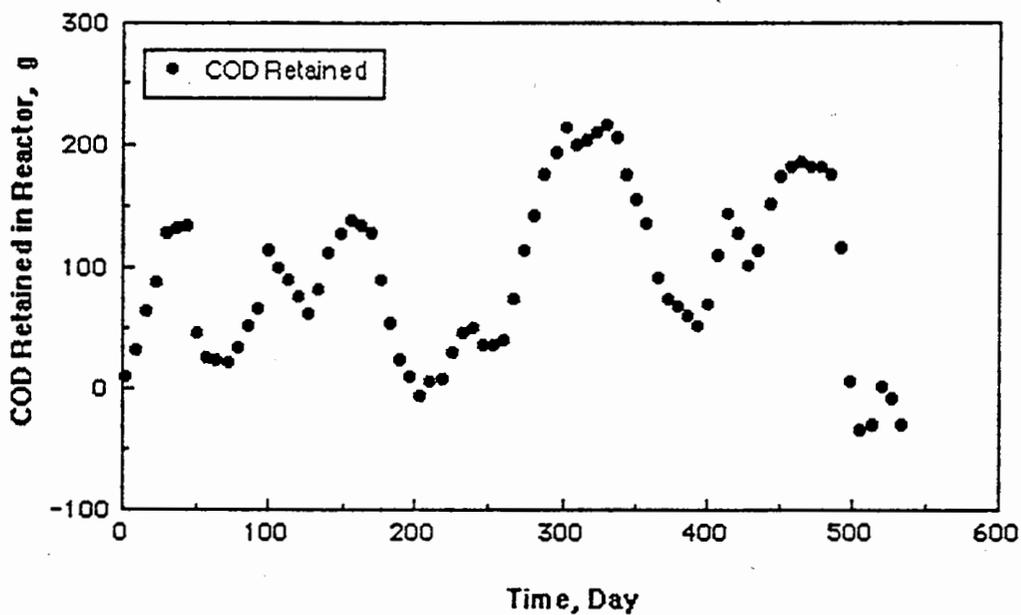


Figure 5. COD Retained in the Reactor as a Function of Time

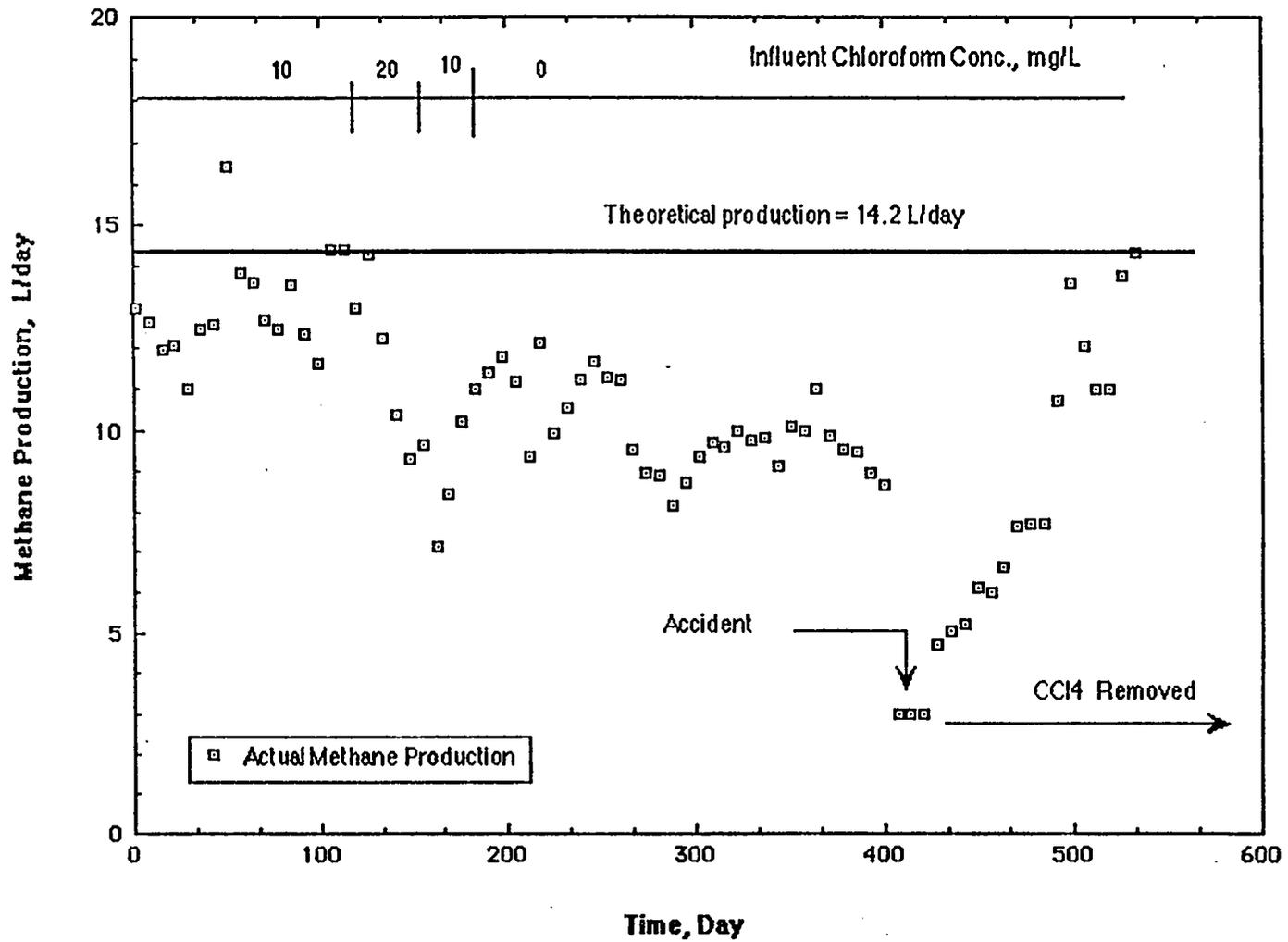


Figure 6. Theoretical vs. Actual Methane Production

sources of chloroform from the feed, gas production increased rapidly to reach the theoretically predicted rate, indicating excellent biodegradation of the background organic compounds, which constituted almost all of the feed COD.

During the acclimation phase and prior to inhibition, acetate was the only detectable background organic compound in the effluent. Neither methanol nor acetone, or its intermediate 2-propanol, was identified in the effluent. The inhibitory phase was characterized by an increase in acetate concentrations and the appearance of acetone and 2-propanol in the effluent. Acetate accounted for 54.5% of the total effluent COD, with acetone and 2-propanol accounting for 40.7% and 3.2%, respectively. Methanol was not detected in the effluent, suggesting that the mechanism degrading methanol to methane was not affected by the levels of chloroform present in the system.

#### FATE OF VOC'S IN THE REACTOR

VOC's fed to a GAC anaerobic reactor can theoretically be removed by either one or a combination of the following mechanisms: adsorption onto the GAC surface, stripping into the gas phase and biological degradation. Hence, these three factors have to be considered when studying the fate of VOC's fed to an anaerobic GAC reactor.

##### Adsorption on the GAC Surface

Adsorption of a compound on GAC is best characterized by an isotherm equation. The isotherm equation for a compound gives the constant temperature equilibrium relationship between the quantity of adsorbate per unit of adsorbent,  $q$ , and the equilibrium concentration of adsorbate in solution,  $C$ . An isotherm is valid only for the concentration range tested. Adsorption isotherms on the same GAC are available in the literature for the VOC's of interest<sup>30</sup> and are summarized in Table 3. These isotherms were derived for single-adsorbate conditions at a constant temperature of 20 °C. The competitive adsorption actually occurring in the reactor due to the presence of other compounds and the higher reactor temperature would result in a reduced capacity of the carbon for the compound from that predicted using the isotherm. The presence of a biofilm around the carbon particle in the reactor may also reduce adsorptive capacity. Hence, the isotherm cannot be used directly to calculate the amount of adsorption of a compound occurring in the reactor. However, it can be used indirectly as an estimate of the maximum adsorption that would occur if adsorption were the sole mechanism of removal. Starting with a hypothetical effluent concentration of 100  $\mu\text{g/L}$  (this value was chosen because it fell within the valid concentration ranges for all the compound isotherms), the equation can be used to calculate the mass loading of that particular compound per unit mass of GAC. This value, when multiplied by the total mass of GAC in the reactor, gives the mass of the compound on the GAC that is in equilibrium with the 100- $\mu\text{g/L}$  effluent concentration. Using actual reactor feed flow rates and effluent concentrations, the time required to load the aforecalculated mass onto the carbon can be determined. This represents the time it would take for the effluent concentration in the reactor to reach 100  $\mu\text{g/L}$  if adsorption were the sole mechanism responsible for removal. As mentioned earlier, the isotherms overestimate the actual capacity of the reactor

Table 3. Adsorption Isotherms for VOC's on Filtrasorb-400 GAC

(After Speth and Miltner<sup>30</sup>)

Temperature = 20°C

<u>Compound</u>	<u>Adsorption Isotherm</u>	<u>Valid Concentration Range (<math>\mu\text{g/L}</math>)</u>
Chloroform	$92.5^*C^{0.669}$	13.2 - 226
Carbon Tetrachloride	$387^*C^{0.594}$	9.1 - 429
Chlorobenzene	$9170^*C^{0.348}$	15.4 - 732
Methylene Chloride	$6.25^*C^{0.801}$	18.1 - 715
Toluene	$5010^*C^{0.429}$	2.3 - 104
Tetrachloroethylene	$1070^*C^{0.604}$	1.2 - 738

carbon because they do not account for the higher reactor temperature and the effect of competitive adsorption. The time value calculated, therefore, represents an upper limit figure. Thus, applying the above assumptions, all of which tend to overestimate the adsorption capacity of GAC for the compound, it would at most take this calculated time for the reactor concentration to reach 100  $\mu\text{g/L}$ . Since, in the absence of biological activity, all the assumptions made in calculating the adsorptive capacity of carbon tend to overestimate capacity, the concentration under actual conditions can only be higher than 100  $\mu\text{g/L}$  at the calculated time. However, as can be seen from Table 4, for all the VOC's except chloroform, effluent concentrations of 100  $\mu\text{g/L}$  were never seen in the reactor. Even for chloroform, the actual reactor concentration first reached 100  $\mu\text{g/L}$  long after theoretically predicted by the pure adsorption calculations. On the basis of these calculations alone, there appears to be sufficient justification for the argument that adsorption was not the sole removal mechanism and that biodegradation of the compounds was also occurring.

Table 4. Comparison of Actual Reactor Performance vs. Pure Adsorption

Reactor Operating Conditions:

Day 1 - Day 76: Feed Concentration of Each VOC = 5 mg/L  
Day 77 - Day 119: Feed Concentration of Each VOC = 10 mg/L  
Day 120 Onwards: Feed Concentration of Each VOC = 20 mg/L\*\*\*  
 Feed Flow Rate = 8.0 L/day  
 Total Period of Reactor Operation = 550 days

Compound	Time to Reach Effluent Conc. of 100 $\mu\text{g/L}$ Assuming Only Adsorption (days)	Time to Reach 100 $\mu\text{g/L}$ in Actual Reactor (days)
Chloroform	76	150
Carbon Tetrachloride	134	Never Reached
Chlorobenzene	505	Never Reached
Methylene Chloride	9	Never Reached
Toluene	417	Never Reached
PCE	240	Never Reached

\*\*\* Except in cases of chloroform and carbon tetrachloride (See Table 3).

### Stripping of VOC's

To determine whether any of the VOC's were being stripped from the effluent by the gas produced in the system, analysis of the gas for VOC's was started on Day 450. All the compounds appearing in the effluent, with the exception of methylene chloride, were detected in the gas phase. This analysis was performed on a regular basis for an extended period of reactor operation, and sufficient data were gathered to enable derivation of a relationship between the mass of compound in the effluent and the mass of compound in the gas. The results of this study are summarized in Table 5.

Table 5. Summary of VOC Stripping Analysis

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<u>Compound</u>	<u>Mass in Gas/Mass in Effluent (g/day)/(g/day)</u>
Vinyl Chloride	3.846
Methylene Chloride	No Stripping in Gas
Chloroform	0.246
TCE	1.137
PCE	0.430

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### Biological Degradation

The effect of biodegradation can be best studied during the phase of no GAC replacement. If no carbon is being replaced, then at steady state, no removal by adsorption will be occurring, and any removal of VOC's is solely due to biodegradation or stripping. The extent of removal by stripping can be calculated as described in the previous section, knowing the effluent concentrations of the VOC's. Hence, a mass balance on each VOC will yield directly the removal that can be attributed to biodegradation. Mass balances were performed for each of the VOC's separately and the results are summarized below.

Methylene Chloride — Steady-state data from the period of zero GAC replacement were utilized to perform a mass balance. The steady-state influent and effluent concentrations were 20 mg/L and 25 µg/L, respectively, which at a flow rate of 8 L/day through the reactor yield influent and effluent mass flow rates of

160,000  $\mu\text{g}/\text{day}$  and 200  $\mu\text{g}/\text{day}$ , respectively. As described in the previous section, no stripping was observed for methylene chloride. Furthermore, as no carbon replacement was being practiced during this period, the effect of adsorptive removal can be neglected, leaving biodegradation as the sole mechanism responsible for the 99.9% removal observed.

Toluene, Chlorobenzene — Effluent toluene and chlorobenzene concentrations were below detection limits throughout the period of no GAC replacement. Using the same argument applied for methylene chloride suggests complete biological removal of these compounds, as no trace of either of these compounds was observed in the gas phase.

Carbon tetrachloride, Chloroform — Chloroform is a biodegradation by-product of carbon tetrachloride; consequently, the mass balances have to be done simultaneously for these compounds. One mole of carbon tetrachloride will biotransform to one mole of chloroform. Thus, in terms of moles of chloroform, the influent molar potential for chloroform equals the sum of the moles of chloroform and carbon tetrachloride in the influent. Stripping characteristics of carbon tetrachloride are not available as the stripping study was conducted after carbon tetrachloride had been removed from the feed. The concentration of carbon tetrachloride in the effluent was almost always below detection levels, and the mass balance for the period when carbon tetrachloride but not chloroform was being fed to the reactor is based on the not unreasonable hypothesis that these negligible effluent concentrations are the result of nearly all the carbon tetrachloride being transformed via chloroform. Conversely, the same negligible effluent concentrations would render insignificant the effect of any stripping that was to occur from the effluent. Steady-state data for this period included a carbon tetrachloride influent concentration of 20 mg/L and no chloroform at a flow rate of 8 L/day. This corresponds to an influent chloroform potential of 1039  $\mu\text{Moles}/\text{day}$ . The effluent steady-state concentration of chloroform was 350  $\mu\text{g}/\text{L}$  with no carbon tetrachloride being detected. At the 8-L/day flowrate, this translates to a molar effluent flow of 19.3  $\mu\text{Moles}/\text{day}$ . Using the factor obtained in the stripping study for chloroform (Table 5), the molar flow rate in the gas amounts to 4.7  $\mu\text{Moles}/\text{day}$ . Thus, a total of 24  $\mu\text{Moles}/\text{day}$  of chloroform can be accounted for in the effluent and gas. As this was a period of no carbon replacement, adsorptive removal can be ruled out. During this period, therefore, it is concluded that 97.7% of the influent chloroform potential was being removed biologically.

Tetrachloroethylene (PCE) — The pathway of biodegradation of PCE is known to be through TCE, DCE, and vinyl chloride. A mass balance on PCE would by necessity, therefore, involve these other compounds as well. The transformation occurs on a one-to-one molar basis; hence, one mole of either TCE, DCE, or vinyl chloride in the effluent corresponds to an equivalent mole of PCE. The influent concentration of 20 mg/L of PCE fed at rate of 8 L/day corresponds to a molar flow rate of PCE of 964  $\mu\text{Moles}/\text{day}$ . The effluent quality corresponding to this steady-state period shows effluent concentrations of 25  $\mu\text{g}/\text{L}$  of PCE, 15  $\mu\text{g}/\text{L}$  of TCE, and 10  $\mu\text{g}/\text{L}$  of vinyl chloride. At a flow rate of 8 L/day through the reactor, this corresponds to molar flow rates of 1.2  $\mu\text{Moles}/\text{day}$  of PCE, 0.9  $\mu\text{Moles}/\text{day}$  of TCE, and 1.28  $\mu\text{Moles}/\text{day}$  of vinyl chloride. The corresponding flow rates in the gaseous phase can be calculated using the factors obtained in

the stripping study and summarized in Table 5. These are 0.52  $\mu$ Moles/day of PCE, 1.02  $\mu$ Moles/day of TCE, and 4.92  $\mu$ Moles/day of vinyl chloride. The above values add up to a combined equivalent PCE molar flow rate of 9.84  $\mu$ Moles/day leaving the reactor in the gas and liquid phases. Again neglecting adsorptive removal based on the zero GAC replacement schedule practiced during this period, the mass balance indicates that 98.9% of the PCE was being removed through complete biological degradation.

#### SUMMARY AND CONCLUSIONS

The objective of this study was to examine the effectiveness of the anaerobic GAC expanded-bed bioreactor as a pretreatment unit for the detoxification of a simulated high strength industrial wastewater containing several volatile RCRA compounds present in backgrounds consisting of non-RCRA organic compounds. As a pretreatment unit, the goal was not to maximize COD destruction but to reduce the VOC concentrations to acceptable levels. This goal was achieved very satisfactorily. The reactor demonstrated excellent treatment; removals of greater than 97% were achieved for all the VOC's. Chloroform was found to be inhibitory to the system at effluent concentrations of about 100  $\mu$ g/L. It was found to inhibit the degradation of acetate and acetone, two of the three base flow organic compounds. Chloroform itself, however, was removed to greater than 97%. The only limiting factor in this treatment study was the high effluent COD experienced during the inhibitory phase, which was composed almost entirely of acetate and acetone and, as such, could easily be removed by any of several treatment options. The amount of stripping occurring was negligible compared to the amount of stripping anticipated to occur in an aerobic biological process. The anaerobic GAC expanded-bed bioreactor represents an excellent pretreatment unit for the treatment of wastes containing VOC's.

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DEVELOPMENT OF NONLINEAR GROUP CONTRIBUTION METHOD FOR PREDICTION OF  
BIODEGRADATION KINETICS FROM RESPIROMETRICALLY-DERIVED KINETIC DATA

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ABSTRACT

The fate of organic chemicals in the environment depends on their susceptibility to biodegradation. Hence, development of regulations concerning their manufacture and use requires information on the extent and rate of biodegradation. Recent studies have attempted to correlate the kinetics of biodegradation with the compound's molecular structure. This has led to the development of structure-biodegradation relationships (SBRs) using the group contribution approach. Each defined group present in the compound's chemical structure is assigned a unique numerical contribution towards the calculation of the biodegradation kinetic constants. In this paper, a non-linear group contribution method has been developed using neural networks, which is trained using literature data on the first order biodegradation kinetic rate constant for a number of priority pollutants. The trained neural network is then used to predict the biodegradation kinetic constant for a new list of compounds, and the results have been compared with the experimental values and the predictions obtained from a linear group contribution method. It has been shown that the non-linear group contribution method using neural networks is able to provide a superior fit to the training set data and produce a lower prediction error than the previous linear method.

## INTRODUCTION

The number and amount of synthetic organic chemicals produced commercially is large and increasing every year. The presence of many of these chemicals in the ecosystem is a serious public health problem. Biodegradation is an important mechanism for removing these chemicals from natural ecosystems. The high diversity of species and the metabolic efficiency of microorganisms suggest that they play a major role in the ultimate degradation of these chemicals (Alexander, 1980). Biodegradation can eliminate hazardous chemicals by biotransforming them into innocuous forms, or completely degrading them by mineralization to carbon dioxide and water.

Kinetic data for calculating biodegradation rates in natural ecosystems are important for several reasons. The computer-based overall fate models, used to estimate the distribution and the concentration of organic compounds in the environment, require rate constants to determine the importance of biodegradation against other competing removal processes, such as volatilization and adsorption. Information regarding the extent and the rate of biodegradation of organic chemicals is very important in evaluating relative persistence of the chemical in the environment, and for regulating their manufacture and use. Due to the large number of chemicals, obtaining this information is labor intensive, time consuming and expensive. Thus, there is a need to develop correlations and predictive techniques to assess biodegradability (Strier, 1980).

Structure-activity relationships (SARs) are used to predict intrinsic properties of many chemicals and to estimate the kinetic constants for important transformation processes. SARs approach can be effectively used to shorten the list of thousands of chemicals to a few hundred key chemicals, for detailed laboratory and field testing. In a recent review of SARs, Nirmalakhandan and Speece (1988) concluded that application of SARs has great potential in predicting the fate of organic chemicals and these techniques are being accepted to a greater extent by regulatory agencies in decision making and policy implementation.

In this paper, a quantitative structure-biodegradation relationship (SBR) has been developed using the group contribution approach. This method is widely used in chemical engineering thermodynamics to estimate pure compound properties such as liquid densities, heat capacities and critical constants.

The group contribution method is similar to the Free-Wilson model widely used in pharmacology and medicinal chemistry. Using this method, a very large number of chemicals can be constituted from perhaps a few hundred functional groups. Using this method, the compound's property is predicted from its molecular structure, which is structurally decomposed into groups or fragments, each group or fragment having a unique contribution towards the specific value of the property.

## TECHNIQUES FOR MEASURING BIODEGRADATION KINETICS

Techniques for evaluating biodegradation kinetics have been reviewed in detail by Howard et al. (1981) and subsequently discussed by Grady (1985). It would be inappropriate to repeat the vast literature incorporated into these two reviews. The essential techniques have been summarized in Table 1 to present their salient features. In the following section, the electrolytic respirometric method will be presented in some detail, since this method was used in obtaining experimental data on biodegradation kinetics utilized in the development of the non-linear model.

### ELECTROLYTIC RESPIROMETRY STUDIES

This study was conducted using an automated continuous oxygen uptake and BOD measuring Voith Sapromat B-12 (12 unit system). The instrument consists of a temperature controlled waterbath, containing measuring units, an on-line microcomputer for data sampling, and a cooling unit for continuous recirculation of waterbath volume. Each measuring unit consists of a reaction vessel, containing the microbial inoculum and test compound, an oxygen generator, comprised of an electrolytic cell containing copper sulfate and sulfuric acid solution, and a pressure indicator which triggers oxygen generation. The carbon dioxide produced is absorbed by soda lime, contained in the reaction flask stopper. Atmospheric pressure fluctuations do not affect the results since the measuring unit forms an air sealed system. The uptake of oxygen by the microorganisms in the sample during biodegradation is compensated by the electrolytic generation of oxygen in the oxygen generator, connected to the reaction vessel. The amount of oxygen supplied by the electrolytic cell is proportional to its amperage requirements, which is continuously monitored by the microcomputer and the digital recorder.

Measurement of oxygen consumption through electrolytic respirometry has been shown to be very promising for automatic data collection associated with biodegradation (Tabak et al, 1984, 1989).

### MATERIALS AND METHODS

The nutrient solution used in our studies was an OECD synthetic medium (1983) consisting of measured amounts per liter of deionized distilled water of (1) mineral salts solution; (2) trace salts solution; and (3) a solution (150 mg/l) of yeast extract as a substitute for vitamin solution.

The microbial inoculum was an activated sludge from The Little Miami wastewater treatment plant in Cincinnati, Ohio, receiving municipal wastewater. The activated sludge sample was aerated for 24 hours before use to bring it to an endogenous phase. The sludge biomass was added to the medium at a concentration of 30 mg/l total solids. Total volume of the synthetic medium was 250 ml in the 500 ml capacity reaction vessels.

The test and control compound concentration in the media were 100 mg/l. Aniline was used as the biodegradable reference compound, at a concentration of 100 mg/l.

In a typical experimental run, duplicate flasks were used for the test compound, and reference compound, aniline, a single flask for toxicity control (test compound plus aniline at 100 mg/l each) and an inoculum control.

The reaction vessels were incubated in the dark at 25° C in the temperature controlled bath and stirred continuously throughout the run. The microbiota of the activated sludge were not pre-acclimated to the substrate. The incubation period of the experimental run was between 28-50 days. A more comprehensive description of the procedural steps involved in the respirometric tests has been presented elsewhere (Tabak et al. 1984, 1989).

## EVALUATION OF BIODEGRADATION KINETICS

In this study, biodegradation was measured by measuring the ratio of the measured biological oxygen demand (BOD) values in mg/l (oxygen uptake values of test compound minus endogenous oxygen uptake values [inoculum control]) to the theoretical oxygen demand (ThOD) of substrate i.e., the ratio BOD/ThOD. The values of theoretical oxygen demand (ThOD) were calculated by using the stoichiometric balanced oxidation equation.

The BOD/ThOD curves calculated from electrolytic respirometric data were characterized by four indices (Urano and Kato, 1986) shown in Figure 1: [1] the lag time ( $t_1$ ) which gives the adaptation time; [2] the rate constant ( $k$ ); [3] the biodegradation time ( $t_d$ ) before the endogenous respiration period; and [4] ratio of BOD/ThOD at time  $t_d$ . The values of  $k$  can be calculated from the slope of the straight line obtained by plotting  $\log(\text{BOD})$  vs time ( $t$ ) for values of  $t$  such that  $t_1 < t < t_d$ . The appropriate equations for calculating the value of  $k$  are given as follows:

$$\begin{aligned} d(\text{BOD})/dt &= k'(\text{BOD}) \\ \log(\text{BOD}) &= (k'/2.3)t = kt + \text{constant}; \quad t_1 < t < t_d \end{aligned}$$

It should be noted that the above kinetic model for obtaining biodegradation kinetics differs from the traditional Monod equation which has been used extensively in the literature to analyze oxygen uptake data. However, the above model was selected for several reasons: [1] it has the ability to represent oxygen uptake data between time  $t_1$  and  $t_d$  by a single parameter ( $k$ ); [2] it follows the method of Urano and Kato model (1986), so that some of their kinetic constant values could be used in our training set; [3] the simple model provided an acceptable fit with the experimental data; and [4] the model results allowed the development of the prediction approach (linear and non-linear) for estimating the kinetic constant values for a variety of test compounds. This allowed us to compare the linear and non-linear approaches using the same data set.

The kinetic constant ( $k$ ) values for the compounds were divided into two sets: [1] the training set; and [2] a testing set. This division of the compound list was based on the criterion that the chemical groups or fragments comprising the testing set compounds were all present in the training set and there were at least 5 compounds in the training set for each chemical group selected.

The main motivation for constructing the training and testing sets was to develop structure-biodegradation relationships using the training set data and then test the relationship using the testing set compounds. A brief review of the literature on structure-biodegradation relationships has been presented in the following section followed by the presentation of the group contribution approach, which was used for analyzing the experimental kinetic constant values.

## STRUCTURE-ACTIVITY RELATIONSHIPS

Structure-activity relationships have been widely used in pharmacology and medicinal chemistry. In the field of biodegradation, interest in structure-activity relationships between the biodegradability of the chemical and its structure started many years ago (Ludzack and Ettinger, 1960). There are several studies which have attempted to correlate some physical, chemical or structural property of a chemical with its biodegradation. Literature reveals both qualitative and quantitative structure-biodegradability correlations. Lyman et al. (1982) summarized rules of thumb which may be used to make qualitative predictions of biodegradability. These rules are based on degree of branching, chain length, oxidation and on number, type and position of substituents on simple organic molecules. Geating (1981) developed a predictive algorithm based on the literature published between 1974 and 1981. Based on the type and the location of substituent groups, the model predicts biodegradability in qualitative terms. The algorithm was applied to group of compounds of known biodegradability and it predicted correctly for 93% of compounds, incorrectly for 2% of compounds and 5% could not be predicted at all. When applied to known nonbiodegradable compounds it was not as successful, predicting 70% correctly and of the remainder roughly half were predicted incorrectly while half could not be predicted at all. Others (Rothkopf and Bartha, 1984, Yoshimura et al., 1980) have also investigated qualitative relationships for certain class of chemicals; however while these studies are useful, none provide the kind of prediction power needed for regulatory decision making, for which quantification is necessary.

Quantitative correlations relating either biodegradation rate constant or 5-day biological oxygen demand (BOD) with different physicochemical properties or rate of other transformation processes have appeared in literature. Most of these correlations are linear single parameter models. Paris and co-workers (1980, 1982, 1983, 1984, 1987) were among the first to investigate quantitative correlations using microbial transformation rate coefficient. They used Monod equation with the assumption that the substrate concentration is less than the half saturation constant so that the transformation rate becomes first order with respect to both substrate concentration as well as microbial concentration. They called this resulting rate coefficient a second order rate coefficient. They investigated several groups of chemicals : pesticides, substituted phthalates, mono-substituted phenols, carboxylic acid esters of 2,4-D, ethyl esters of chlorine substituted acetic acids and substituted anilines. These studies were conducted either with pure culture or mixed populations of organisms from natural environment. In almost all cases they obtained good correlations with a particular property of the chemicals. In case of substituted anilines and mono-

substituted phenols, transformation rate was related with the van der Waal's radii of the substituent groups. The transformation rate in case of phthalates and pesticides was correlated with their alkaline hydrolysis rate constant. They attempted to correlate the rates of carboxylic acid esters of 2,4-D and ethyl esters of chlorine substituted acetic acids with the lipophilicity, specifically octanol-water partition coefficients. They were successful with the first group but not with the second.

Reinke and Knackmuss (1978) studied di-oxygenation of substituted benzoic acids by two species of *Pseudomonas* and were able to obtain a good correlation of the rate coefficient with the Hammett constant for one species but not for the other. Pitter (1984) obtained a linear relation between the logarithm of the biological degradation rate of substituted phenols and anilines and the Hammett constant of the substituent. Of all the substituents (OH, CH<sub>3</sub>, Cl, NO<sub>2</sub> and NH<sub>2</sub>), only the amino group led to deviations from the linear correlations for mono-substituted phenols. He also attempted correlations using the steric and lipophilic constants but failed.

Vaishnav et al. (1987) correlated biodegradation of 17 alcohols and 11 ketones as well as a series of alicyclic chemicals with octanol-water partition coefficient, log P. Alcohols revealed a biphasic relationship with an apparent change in slope at a log P of about 3. The relationship for ketones was parabolic or bilinear with a peak at a log P value of about 1. Statistically the difference between the parabolic and bilinear relationships was marginal, but the bilinear model gives a closer fit to experimental data. Degradability of the hydrophilic members of alicyclics was apparently not related to log P but degradability of the more hydrophobic members decreased with increasing lipophilicity. Banerjee et al. (1984) studied biodegradation of phenol, resorcinol, p-cresol, benzoic acid and various chloro derivatives of phenol, resorcinol and anisole. The biodegradation rate was related to lipophilicity, where the rate increased with decreasing lipophilicity and then levelled off for chemicals with log P less than 2.

Deardan and Nicholson (1986) studied aromatic and aliphatic amines, phenols, aromatic and aliphatic aldehydes, carboxylic acids, halogenated hydrocarbons and amino acids. They calculated different parameters for each compound; molecular connectivities up to seventh order, log P values, molecular volume, accessible molecular surface area, Sterimol steric parameters and atomic charges. They correlated 5-day BOD of these compounds with the atomic charge difference across the bond(s) common to all compounds in the series. The regression coefficient and the constant term for each of the series of compounds were close enough to combine all the data into a single, all embracing equation covering amines, phenols, aldehydes, carboxylic acids, halogenated hydrocarbons and amino acids.

Another approach is to seek direct correlation between biodegradation and molecular structure of the chemical. The structural features of a molecule such as shape, size, branching and nature of atom-atom connections are expressed in terms of numerical descriptors called topological indexes. Many such indexes have been proposed, but the most successful of them in SAR are molecular connectivity indexes, which were introduced by Randic (1975) and then developed extensively by Kier and Hall (1976). Govind (1987) has

correlated first order biodegradation rate constants of priority pollutants with the first order molecular connectivity index. Boethling (1986) has correlated log rate constant for 2,4-D alkyl esters, log percent degraded for carbamates, log percent theoretical oxygen demand for dialkyl ethers, rate constant for dialkyl phthalates and percent theoretical oxygen demand for aliphatic acids with molecular connectivity indexes. All these were single variable models. Two variable models substantially improved results for aliphatic alcohols and acids.

Most of the correlations that have appeared in literature are single parameter relations applicable to a particular class of compounds. This demonstrates that correlations are possible, but also that single parameter correlations are limited in their applicability. Babeu and Vaishnav (1987) calculated 5-day BOD for 45 organic chemicals including alcohols, acids, esters, ketones and aromatics. The BOD data were correlated with water solubilities, log P, molar refractivities and volumes, melting and boiling points, number of carbon, hydrogen and oxygen atoms, molecular weight and theoretical BOD of chemicals. The experimental BOD values for 43 additional chemicals were compared with values predicted by the model and for 84%-88% of the test chemicals prediction was within 80% of the experimental values. Desai et al. (1990) have predicted first order biodegradation rate constants within 20% of the experimental values using group contribution approach. The model based on group contributions was a first order linear model which neglected the interactions between groups. Table 2 summarizes the work done in SARs for predicting the biodegradability of chemicals.

#### GROUP CONTRIBUTION APPROACH

Using a group contribution approach, a very large number of chemicals of interest can be constituted from perhaps a few hundred functional groups. The prediction of the property is based on the structure of the compound. According to this method, the molecules of a compound are structurally decomposed into functional groups or their fragments, each having a unique contribution towards the compound property. The advantage of this approach is that the molecules of the compounds may be structurally dissected in any convenient manner and no independently measured group constants are required in the analysis.

The biodegradability rate constant,  $k$ , can be expressed as a function of contribution  $\alpha$ , of each group or fragment of the compound

$$\ln(k) = f(\alpha_1, \alpha_2, \dots, \alpha_j)$$

In general, the above functional relationship can be classified into two types: [1] linear function; and [2] non-linear function.

#### LINEAR GROUP CONTRIBUTION METHOD

The above general function can be expanded in terms of Taylor series. If the terms from second order onwards are neglected, a linear first order

model for biodegradation rate constant  $k$  (1/hr) is obtained and this can be expressed as:

$$\ln(k) = \sum_{j=1}^L N_j \alpha_j$$

where  $N_j$  is the number of groups of type  $j$  in the compound,  $\alpha_j$  is the contribution of group of type  $j$  and  $L$  is the total number of groups in the compound. For each compound a linear equation in  $\alpha$ 's is constructed. This generates a series of linear equations for a given data set which are solved for  $\alpha$ 's, using the method of least squares.

The above model, being first order approximation, will break down if interaction between groups become important. The interaction of different groups can be treated by considering second and higher order terms of the series.

Data generated by Urano and Kato (1986) using electrolytic respirometry was used in applying the linear group contribution method. This ensured that the test conditions for obtaining the data were the same for all the compounds. The experimental conditions used by Urano and Kato (1986) were: temperature 20° C, pH of solution 7, sludge concentration 30 mg/l and compound concentration 100 mg/l.

Urano and Kato (1986) had obtained data [kinetic constant ( $k$ ) values] for 74 compounds in their study. However, in our analysis using the linear group contribution method, it was necessary to ensure that each group, considered in the analysis, occurred in at least 5 compounds in the training set. This requirement prevented us from using the entire set of compounds studied by Urano and Kato (1986), and only 18 compounds were used for calculating the group contribution values for 8 groups. The compounds used in our analysis (training set) were: ethyl alcohol, butyl alcohol, ethylene glycol, acetic acid, propionic acid, n-butyric acid, n-valeric acid, adipic acid, methyl ethyl ketone, hexamethylenediamine, n-hexylamine, mono-ethanol-amine, acetamide, benzene, benzyl alcohol, toluene, acetophenone, and aminophenol. The experimental values of the kinetic constants for these chemicals have been tabulated in Table 3.

The group contribution parameters for all the groups considered in the analysis are given in Table 4, which are modified since previous work (Desai et al. 1990). Note these contribution values are used for calculating the value of  $\ln(k)$  rather than the kinetic constant ( $k$ ) itself.

To validate the results, experiments were conducted by the authors using an electrolytic respirometer (Voith-Morden, Milwaukee, WI) for cresols, phenol, 2,4-dimethyl phenol and butyl benzene. These compounds, obtained from Aldrich chemical company, were of 99+% purity. Except for the source and nature of biomass, the experimental conditions were the same as used by Urano and Kato (1986).

The oxygen uptake data was analyzed using the kinetic model presented earlier, and the best fit kinetic constant (k) value was obtained for each compound in the testing set. The experimental k values obtained for the test compounds are given in Table 3.

#### NON-LINEAR GROUP CONTRIBUTION OR NEURAL NETWORK METHOD

To incorporate the effects of interactions between the chemical groups used in the group contribution approach, it was necessary to develop a non-linear method. It was important that the non-linear method included not only all the interactions between the groups but also the algebraic form (type of non-linearity, such as square, cubic, etc.) of such interactions. Since this information was not known a priori, a neural network model was used to include all possible interactions between the groups and the algebraic form of these interactions was implicitly determined from the training set data using a large number of adaptable parameters or network weights.

#### NEURAL NETWORK MODELS

There is extensive literature on mathematical models of artificial neural networks, beginning with the work of McCulloch and Pitt (1943), Hebb (1949), Rosenblatt (1959), Widrow (1960) and Posch (1968). Recent work by Hopfield (1982, 1984, 1986), Rumelhart, et al (1986), Sejnowski and Rosenberg (1986), Feldman and Ballard (1982), and Grossberg (1986) has revived interest in the field of artificial neural nets. Neural networks have found applications in image and speech recognition, on-line diagnosis of process faults, process control and in optimization of complex functions.

Artificial neural network models consist of many nonlinear computational elements operating in parallel and arranged in patterns similar to biological neural nets. The nodes or computational elements are connected via weights that are typically adapted during use to improve performance (Lippmann, 1987). Superior performance is achieved via dense interconnection of simple computational elements.

Computational elements or nodes used in neural net models are nonlinear. In our model, each node, shown schematically in Figure 2, has a large number of inputs and a single output. Each input value has an associated activation and weight. Each node or computational element applies an activation function to the sum of the products of the input activations and weights, and thereby generates the output value. The output of each computational element or node can be expressed as follows:

$$O_{pj} = 1/[1 + \exp[-(\sum W_{ji}O_{pi} + \theta_j)]]$$

where  $O_{pj}$  = output value of node j  
 $O_{pi}$  = output value of node i  
 $W_{ji}$  = connection weight between the ith and jth nodes  
 $\theta_j$  = bias of the jth node

Hence, each node or computational element forms a weighted sum of N inputs and passes the result through a nonlinearity, mathematically expressed by the

above equation. Figure 3 is a plot of this sigmoidal nonlinearity, inherent in each node. More complex neural network models may include temporal integration or other types of time dependencies and more complex mathematical operations.

The neural network consists of interconnected nodes or computational elements. In our study, a three layer neural network was used, with eight input nodes, eight hidden or intermediate layer nodes, and one output node, as shown in Figure 4. It consists of a hidden or intermediate layer between the input and output nodes. Multi-layer neural networks overcome some of the limitations of the single layer models. The capabilities of multi-layer neural networks stem from the nonlinearities used within nodes, which allow arbitrarily complex decision regions.

The neural network was trained by using a back-propagation algorithm, which used a gradient search technique to minimize a cost function equal to the mean square difference between the desired and the actual net outputs. The desired output of all nodes is typically "low" (0 or < 0.1) unless that node corresponds to the class the current input is from, in which case its output is "high" (1.0 or > 0.9). The net is trained by initially selecting small random weights and internal thresholds and then presenting the training data (number of each type of chemical groups present and the experimentally measured biodegradation kinetic rate constant) for each chemical repeatedly. Weights are adjusted after each trial, until the weights converge and the cost function is reduced to an acceptable value.

The output of the network depends on the weights assigned to each connection between the layers. Training of the network corresponds to the assignment of weights, which are determined in the back-propagation algorithm by minimizing the error function,  $E_p$ , written as follows

$$E_p = 1/2 \sum (t_{pj} - o_{pj})^2$$

where  $t_{pj}$  and  $o_{pj}$  are the desired and actual activation values of the output node  $j$ , due to an input pattern  $p$ . The generalized back propagation algorithm was used by Rumelhart et al (1986) to obtain the minimum value of  $E_p$ . In the first step an input pattern is presented and propagated forward through the network to compute the output value  $o_{pj}$  for each node. The output is compared with the desired value, resulting in an error  $\delta_{pj}$  for each output. For nodes in the output layer, the error signal is given by

$$\delta_{pj} = (t_{pj} - o_{pj})o_{pj}(1-o_{pj})$$

The error signal for a node in the intermediate layer is given by

$$\delta_{pj} = o_{pj}(1-o_{pj}) \sum \delta_{pk}W_{kj}$$

In the second step, a backward pass is made through the network and the error signal is passed to each node in the network and the appropriate weight changes are made using the following equation

$$W_{ij}(t+1) = W_{ij}(t) + \beta (W_{ij}(t) - W_{ij}(t-1))$$

where  $\beta$  is the learning rate. In our study, a relatively fast learning rate ( $\beta$ ) of 0.5 was chosen.

In our study, there were eight input nodes, each node corresponding to a specific chemical group, previously used in the linear group contribution analysis, and listed in Table 4. The inputs to the neural network corresponds to the number of each type of chemical group present in the chemical structure. For example, in the case of ethyl alcohol, there are one methyl group, one methylene group, and one hydroxy group. The number of each group is entered corresponding to the node representing the group. The output is the biodegradation kinetic constant value. The data used to obtain the group contributions in the linear group contribution analysis were used for training the neural network.

## RESULTS AND DISCUSSION

For the training set compounds, listed in Table 3, Table 5 presents the results of the linear group contribution analysis and the nonlinear group contribution or neural network approach. It shows the goodness of fit between the experimental values and the computed values. It can be seen that the mean error in the linear group contribution method is generally larger than the neural network method. Figure 5 provides a comparison between the experimental and predicted (calculated) biodegradation kinetic data by neural network and linear group contribution.

Table 6 lists the results for the testing set compounds. This shows the ability of the method to predict the kinetic constant value for compounds that were not in the training set.

Both the linear group contribution and the neural network methods are unable to distinguish between the ortho-, meta- and para-cresols since the position of the hydroxy group was not considered in the analysis. The error between the predicted and experimental values are generally lower by the neural network method when compared with the linear group contribution method. However, further testing of these methods is needed before any concrete conclusions regarding these methods can be drawn.

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**Table 1: Summary of Techniques for Evaluating Biodegradation Kinetics**

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Type of Reactor	Comments
Continuous	Requires an acclimated biomass Time consuming to operate Several steady-state conditions have to be investigated Requires several samples Provides data only in the non-inhibitory range for inhibitory substrates Can be operated in several configurations to simulate real plants
Batch	Can be used with either acclimated or unacclimated biomass Can be used for determining kinetic parameters
Fed-Batch	Requires acclimated biomass Requires specific assay for test compound Provides only relative value for kinetic parameter

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Table 2. Background Summary for SAR

Author(s)	Year	Parameters	Comments/Compounds Studied
<u>QUALITATIVE</u>			
Lyman, et al.	1982	-	summarized rules of thumb
Geating	1981	-	developed qualitative predictive algorithm
<u>QUANTITATIVE</u>			
Reineke and Knackmuss	1978	Hammett constant of substituent	substituted benzoic acids
Wolfe, et al.	1980	Alkaline hydrolysis rate constant	phthalate esters and pesticides
Paris, et al	1982, 1983	van der Waal's radii of substituent	substituted phenols
Banerjee et al	1984	Hammett constant of substituent	phenols and their chloro derivatives
Paris, et al	1984	octanol-water partition coefficient	esters of chlorinated carboxylic acids
Pitter	1984	Hammett constant of substituent	substituted phenols and anilines
Boethling	1986	molecular connectivity	2,4-D alkyl esters, carbamates, alkyl ethers, dialkyl phthalates and aliphatic acids
Deardan and Nicholson	1986	atomic charge difference	amines, phenols, alde-, hydes, carboxylic acids, halogenated hydrocarbons and amino acids
Babeu and Vaishnav	1987	theoretical BOD of compounds, melting	alcohols, acids, esters, ketones and aromatics point and number of Multiparameter model carbon atoms
Govind	1987	molecular connectivity	priority pollutants

Table 2 continued..

Author(s)	Year	Parameters	Comments/Compounds studied
Paris and Wolfe	1987	van der Waal's radii of substituent	substituted anilines
Vaishnav, et al	1987	octanol-water partition coefficient	alcohols, ketones and alicyclics
Desai, et al	1990	group contribution parameters	various priority pollutants

TABLE 3. Training and Testing Dataset

Compound	Ln(k)	Average Ln(k)
<b>Training Set</b>		
Ethyl alcohol	-2.90 ~ -3.15	-3.02
Butyl alcohol	-3.08 ~ -3.32	-3.19
Ethylene glycol	-3.35 ~ -3.65	-3.49
Acetic acid	-2.60 ~ -2.72	-2.66
Propionic acid	-2.67 ~ -2.97	-2.81
n-Butyric acid	-2.70 ~ -3.06	-2.87
n-Valeric acid	-2.63 ~ -2.66	-2.65
Adipic acid	-2.81 ~ -3.12	-2.96
Methyl ethyl ketone	-3.47 ~ -3.69	-3.58
Hexamethylenediamine	-4.34 ~ -4.51	-4.43
n-Hexylamine	-2.86 ~ -3.06	-2.96
Mono-ethanolamine	-3.32 ~ -3.38	-3.35
Acetamide	-3.00 ~ -3.06	-3.03
Benzene	-2.86 ~ -2.98	-2.92
Benzyl alcohol	-2.78 ~ -3.17	-2.96
Toluene	-2.60 ~ -2.86	-2.73
Acetophenone	-3.17 ~ -3.54	-3.34
Aminophenol	-3.24 ~ -3.30	-3.27
<b>Test Set</b>		
o-Cresol	-2.57 ~ -2.81	-2.69
m-Cresol	-2.23 ~ -2.51	-2.37
p-Cresol	-2.34 ~ -2.60	-2.47
Phenol	-2.83 ~ -3.17	-3.00
2,4-Dimethyl phenol	-2.63 ~ -3.07	-2.85
Butylbenzene	-2.99 ~ -3.27	-3.13

TABLE 4. Groups and Their Contribution Values

Group		$\alpha_j$
Methyl	CH <sub>3</sub>	-1.28
Methylene	CH <sub>2</sub>	-0.12
Hydroxy	OH	-1.54
Acid	COOH	-1.24
Ketone	CO	-0.59
Amine	NH <sub>2</sub>	-1.63
Aromatic CH	ACH	-0.48
Aromatic carbon	AC	0.93

Table 5. Comparison of Experimental and Predicted  $\ln(k)$  for Training Set

Compound	$-\ln(k)$	$-\ln(k)$	%Error	$-\ln(k)$	%Error
	Experimental	Neural Network		Linear Method	
Ethyl alcohol	3.02	3.01	0.33	2.97	1.43
Butyl alcohol	3.19	3.16	0.94	3.24	1.30
Ethylene glycol	3.49	3.45	1.15	3.39	2.87
Acetic acid	2.66	2.68	0.75	2.49	6.55
Propionic acid	2.81	2.81	0.06	2.65	5.84
n-Butyric acid	2.87	2.83	1.39	2.75	4.17
n-Valeric acid	2.65	2.70	1.89	2.88	8.86
Adipic acid	2.96	2.93	1.01	2.94	0.55
Methyl ethyl ketone	3.58	3.63	1.40	3.31	11.90
Hexamethylene diamine	4.43	4.22	4.74	3.96	10.43
n-Hexylamine	2.96	2.97	0.33	3.52	19.11
Mono-ethanolamine	3.35	3.38	0.90	3.41	1.80
Acetamide	3.03	3.01	0.66	3.48	15.19
Benzene	2.92	2.94	0.68	2.87	1.62
Benzyl alcohol	2.96	2.94	0.68	3.12	5.57
Toluene	2.73	2.70	1.10	2.70	1.10
Acetophenone	3.34	3.31	0.90	3.33	0.38
Aminophenol	3.27	3.29	0.61	3.13	4.26

Table 6. Comparison of Experimental and Predicted  $\ln(k)$  for Testing Set

Compound	$-\ln(k)$ Experimental	$-\ln(k)$ Neural Network	%Error	$-\ln(k)$ Linear Method	%Error
o-Cresol	2.69	2.62	2.02	2.87	6.59
m-Cresol	2.37	2.62	10.74	2.87	20.92
p-Cresol	2.47	2.62	6.46	2.87	16.24
Phenol	3.00	2.91	3.17	2.99	0.29
2,4-Dimethyl phenol	2.85	2.58	9.29	2.74	3.82
Butylbenzene	3.13	3.18	1.53	3.10	5.84

Key words - Structure-activity relationships, Biodegradation kinetics, Respirometry, Group contribution method, Neural networks

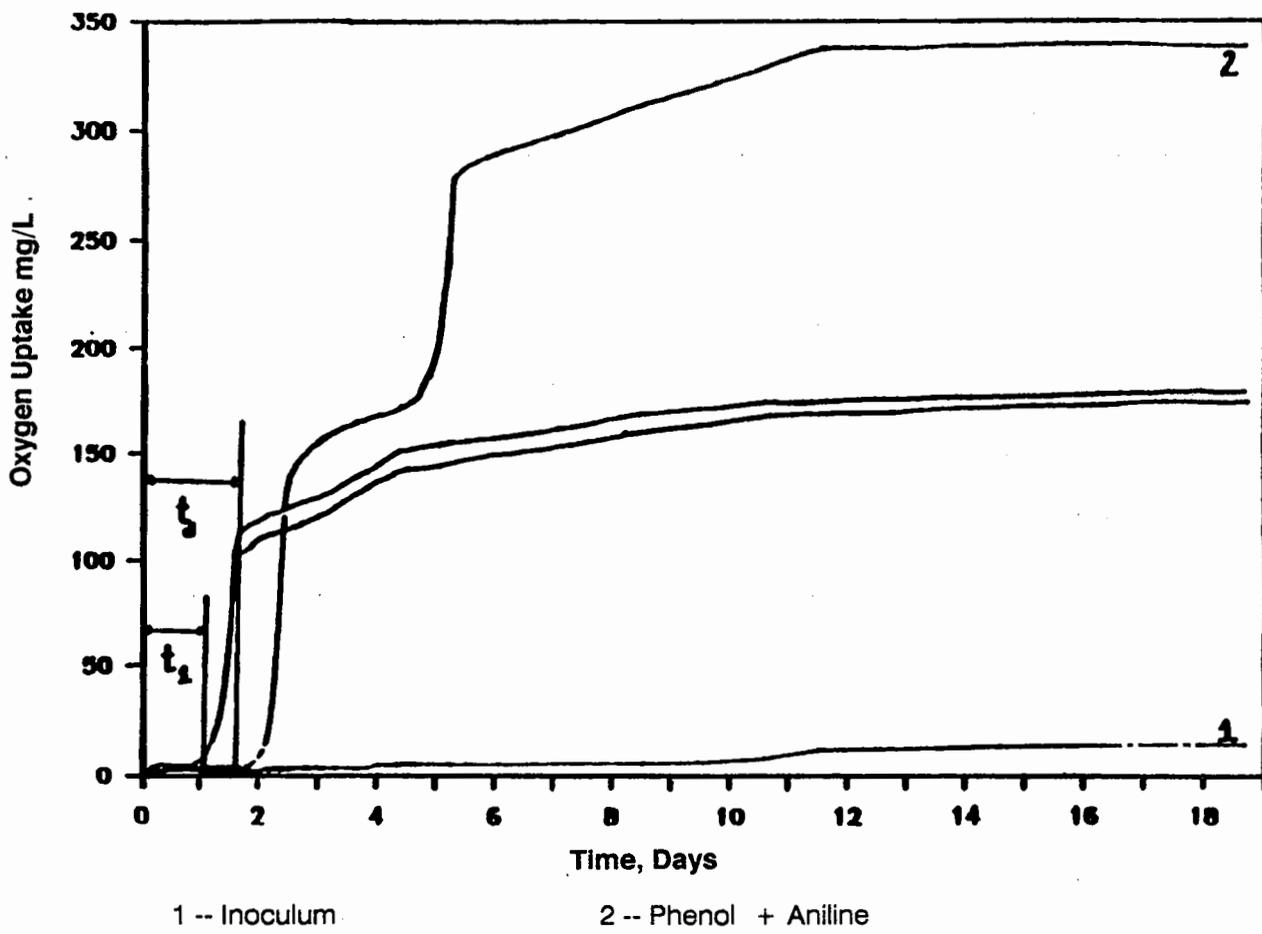


Figure 1. Oxygen Uptake of Phenol

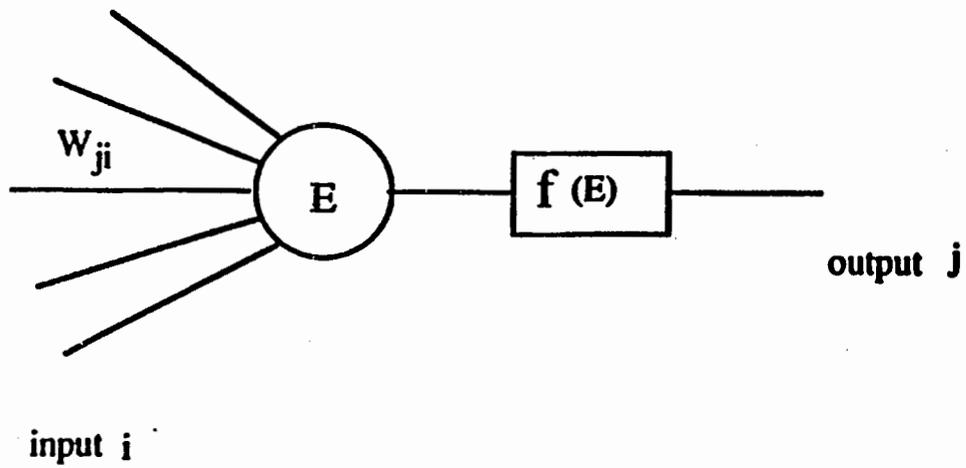


Figure 2. Processing element

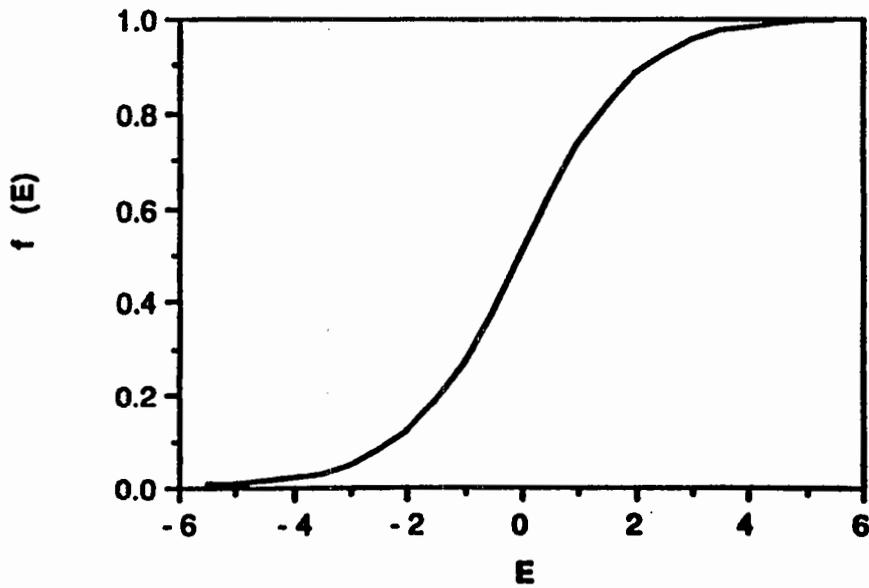


Figure 3. Sigmoid logistic function

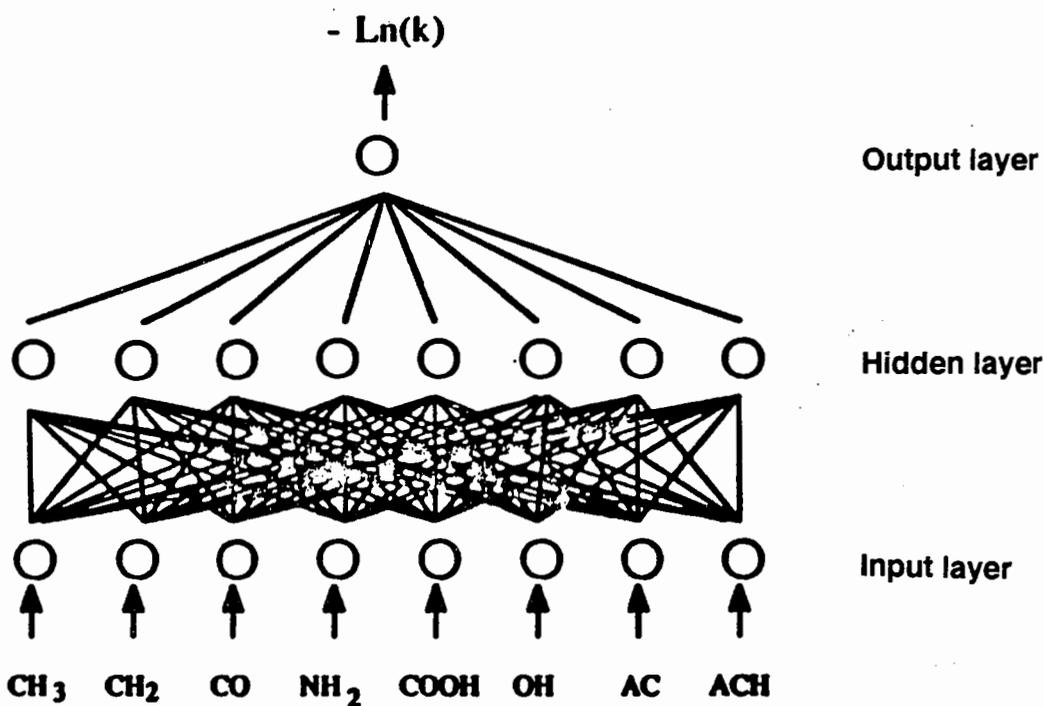


Figure 4. Neural network architecture used to evaluate  $-\text{Ln}(k)$

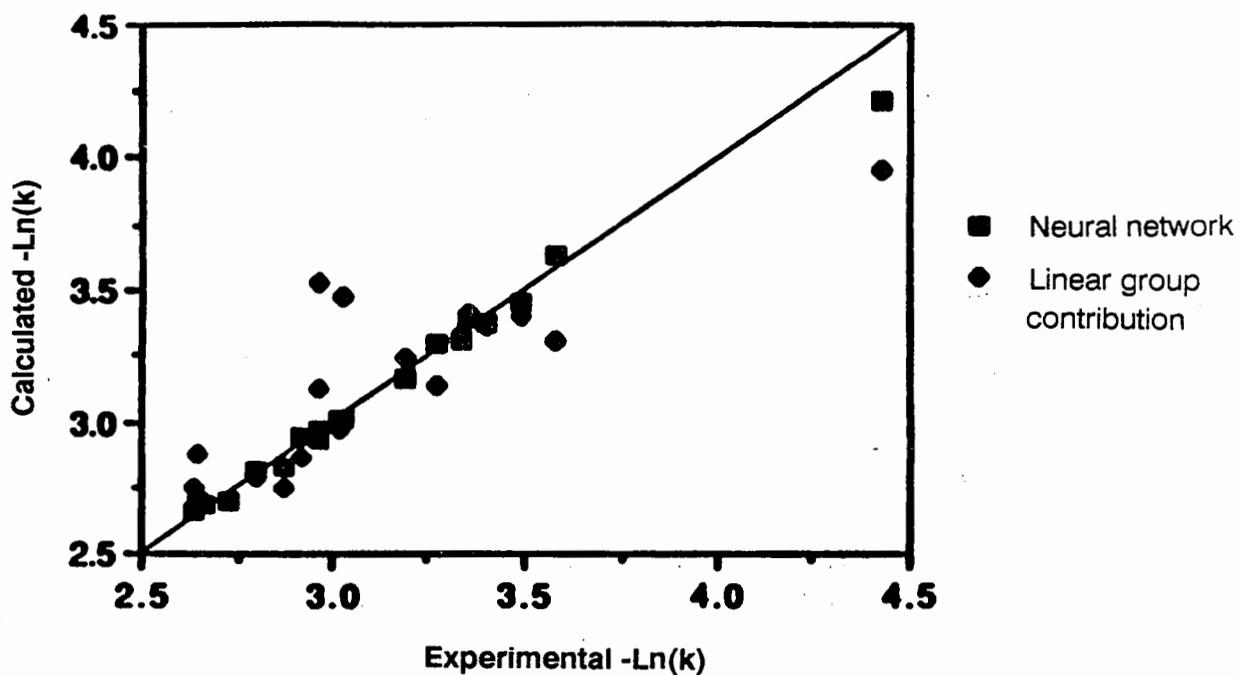


Figure 5. Comparison of experimental  $-\text{Ln}(k)$  by neural network and linear group contribution method

THE EFFECT OF CHLORINE ON NO<sub>x</sub> EMISSIONS FROM THE INCINERATION OF  
NITROGEN-CONTAINING WASTES

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ABSTRACT

Combustion of organo-chlorides, chlorinated salts, and chlorinated acids are unique to incineration systems. Many of these chlorinated species are processed in hazardous waste incinerators as principal organic hazardous constituents (POHCs), or in aqueous solutions containing other POHCs. In municipal waste and hospital waste incinerators, chlorinated plastics constitute sizeable fractions of the total waste streams. Numerous examinations have been conducted in recent years that have sought to characterize the incineration of chlorinated wastes as well as to determine possible chlorinated products of incomplete combustion (PICs). However, although the effect of halogens on flame chemistry has been studied previously, little is known regarding chlorine's effects on other pollutants such as NO<sub>x</sub> from fuel-bound nitrogen.

Experiments are being conducted on a 83 kW (280,000 Btu/hr) tunnel combustor to quantify and understand any effect of fuel chlorine content on NO<sub>x</sub> formation. The bench-scale combustor is a horizontal refractory-lined cylinder with a quartz window for flame visualization, and multiple ports for in-flame and post-flame sampling. A movable-block International Flame Research Foundation (IFRF) type variable swirl burner with interchangeable gaseous and liquid fuel nozzles is capable of providing near-burner zone aerodynamic simulation of various flame types.

It is hypothesized that chlorine may act to inhibit NO formation through its interaction with free radical species. Preliminary results co-firing aqueous solutions of NH<sub>4</sub>OH (2.5% fuel nitrogen) and HCl with natural gas indicate a 30% reduction in NO emissions as fuel chlorine concentrations are increased from 0 to 2.5%. Additional tests are currently being conducted to examine pyridine (C<sub>5</sub>H<sub>5</sub>N) and chlorinated alkane (CCl<sub>4</sub> and C<sub>8</sub>H<sub>17</sub>Cl) combustion in a No. 2 fuel oil flame. Other system parameters (furnace load, preheat air temperature, stoichiometric ratio, and flame type) as well as air staging for NO<sub>x</sub> control are also being examined. These results, and their interpretation through kinetic modeling will be presented.

PILOT-SCALE EVALUATION OF AN INCINERABILITY RANKING  
SYSTEM FOR HAZARDOUS ORGANIC COMPOUNDS

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ABSTRACT

The U.S. EPA's hazardous waste incinerator performance standards specify a minimum destruction and removal efficiency (DRE) for principal organic hazardous constituents (POHCs) in the incinerator waste feed. In the past, selection of appropriate POHCs for incinerator trial burns has been based largely on their heats of combustion. Attempting to improve the system by which trial burn POHCs are selected, the University of Dayton Research Institute, under contract to EPA, has developed a thermal-stability-based ranking of compound "incinerability". The subject study was conducted to evaluate the laboratory-developed ranking system in a pilot-scale incinerator.

A mixture of 12 POHCs, spanning the ranking scale from most- to least-difficult to destroy (Class 1 to Class 7, respectively), was combined with a clay-based sorbent matrix, and fed into the rotary kiln incineration system at the U.S. EPA Incineration Research Facility. In a series of 5 tests, the following conditions were evaluated: nominal/typical operation; thermal failure (quenching); mixing failure (overcharging); matrix failure (low feed H/Cl ratio); and a worst-case combination of the 3 failure modes.

Under nominal conditions, mixing failure, and matrix failure, kiln exit DREs for each compound were comparable from test to test. Operating conditions in these 3 modes appeared to be sufficient to effect considerable destruction (>99.99% DRE) of all 12 compounds. As a result, separation of the highest ranked POHCs from the lowest ranked POHCs according to observed DRE was not possible; a correlation between POHC ranking and DRE could not be identified.

The correlation between predicted and observed incinerability was stronger for the thermal failure and worst-case conditions. Kiln exit DREs for the four most difficult-to-destroy POHCs (those in Classes 1 and 2) ranged from 99% to 99.99% under these conditions, and were generally lower than DREs for the higher class POHCs.

## U.S. EPA INCINERATION RESEARCH FACILITY UPDATE

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### ABSTRACT

In FY'89, the physical plant of the EPA's Incineration Research Facility (IRF) in Jefferson, Arkansas, underwent a major expansion. The building was enlarged and many components of the rotary kiln incinerator system (RKS) were upgraded. In FY'90, the IRF's RCRA permit was modified and reissued to include the expanded facility. The IRF's capabilities were further upgraded to meet the increasing demand for incineration research at the Facility. These improvements included installing an automatic process control system; installing a new kiln ash removal system; installing a scrubber liquor heat exchanger; and reconfiguring the venturi/packed-column scrubber. Together with the single-stage ionizing wet scrubber, the RKS now has the flexibility of two air pollution control systems (APCSs) installed in parallel. Efforts are ongoing to upgrade the continuous emission monitor sampling system, the kiln drive system, and the waste feed system. Onsite laboratory capabilities were also expanded with the addition of an ion chromatograph.

With the completion of the facility upgrade, the pace of testing at the IRF has accelerated. Completed tests include a program to evaluate the principal organic hazardous constituent (POHC) incinerability ranking developed by researchers at the University of Dayton Research Institute; low temperature desorption treatability testing with a soil from a Region II Superfund site; an extensive incineration treatability test series with contaminated soils from a Region III Superfund site; and a test program to evaluate the applicability of incineration as best demonstrated available technology (BDAT) for treating listed waste K088, spent potliner from the production of aluminum.

Planned programs include further testing to support EPA Regional Office Superfund Site remediation efforts; a third series of trace metals tests using a Calvert Scrubber as the APCS; further testing to evaluate the applicability of the POHC incinerability ranking; and potential third party testing as provided for by the Federal Technology Transfer Act.

## INDUSTRY POLLUTION PREVENTION GUIDES

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### ABSTRACT

The Pollution Prevention Research Branch of the U.S. EPA's Risk Reduction Engineering Laboratory is publishing a series of industry-specific pollution prevention guides based on audit reports compiled for the State of California, Department of Health Services. During 1990 EPA published seven guides covering the following industries and commercial sectors: paint manufacturing, pesticide formulating, commercial printing, fabricated metal, selected hospital waste streams, research and education institutions, and printed circuit board manufacturing. Scheduled for publication in early 1991 are guides for an additional six industrial categories: photoprocessors, marine maintenance and repair, pharmaceutical preparation, auto body refinishing, automotive repair, and fiberglass reinforced and composite plastics manufacturing. The presenter will discuss how the guides were developed, outline the waste minimization assessment procedure for selected industry categories, and summarize key findings from the 1991 guides.

INORGANIC RECYCLING/DELCO REGION V HAZARDOUS WASTE RECYCLING DETERMINATION

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ABSTRACT

Inorganic Recycling, Inc. (IR) proposed the use of a thermal process to produce ceramic materials from industrial wastewater treatment sludges. In conjunction with Delco Products in Kettering, Ohio, equipment was developed to make abrasive material from a chromium-bearing electroplating sludge (RCRA waste code F006). IR and Delco Products believed that the new process represented recycling rather than treatment of hazardous waste, and thus was exempt from RCRA permitting requirements.

USEPA's Region V and the Ohio EPA informed IR that the company needed to substantiate the claim that their process constitutes recycling. Guidance was provided from USEPA's Office of Solid Waste on criteria for legitimate recycling of hazardous waste, and the Risk Reduction Engineering Laboratory provided technical assistance in developing and monitoring a series of tests for the process. Upon completion of the tests, Region V and Ohio EPA determined that the system meets the criteria for recycling hazardous waste under RCRA regulations.

NEW JERSEY/EPA WASTE MINIMIZATION ASSESSMENTS

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ABSTRACT

The use of pollution prevention concepts as an approach to reducing the quantities of hazardous and non-hazardous wastes which would otherwise require costly treatment or disposal is receiving increased attention by industry, the public and regulatory agencies. A cooperative effort between the EPA's Risk Reduction Engineering Laboratory (RREL), the New Jersey Department of Environmental Protection (NJDEP), and the New Jersey Institute of Technology (NJIT) has been undertaken to encourage the application of waste minimization approaches and techniques at various facilities within the State of New Jersey. The basis for the effort is the EPA's Waste Minimization Opportunity Assessment Manual (625/7-88/003) which documents a step-by-step approach to conducting assessments and leads to identifying opportunities for improvement. NJIT is applying the Manual at volunteer facilities and assisting them in conducting the assessments in a self-audit approach. Assessments are being conducted at thirty facilities covering ten industry categories. This poster will present the findings of the first five assessments which have been completed by NJIT. The five assessments include 1) a printing operation, 2) a transportation maintenance facility, 3) a finished leather manufacturer, 4) a nuclear powered electrical generating station, and 5) a school district (K-12).

## ASBESTOS CONTROL IN BUILDINGS

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### ABSTRACT

Asbestos Containing Material (ACM) has been used extensively in schools and other buildings. The concern about exposure to asbestos in buildings is based on evidence linking various respiratory diseases with occupational exposure in the shipbuilding, mining, milling and fabricating industries. The presence of asbestos in a building does not mean that the health of building occupants is endangered. If ACM remains in good condition and is unlikely to be disturbed, exposure will be negligible. However, when ACM is damaged or disturbed, asbestos fibers may be released. These fibers can create a potential hazard for building occupants. The methods for asbestos abatement are removal, enclosure, and encapsulation. If ACM is found in a building, a special Operations and Maintenance (O&M) Program should be implemented as soon as possible. The Risk Reduction Engineering Laboratory (RREL) Program for asbestos addresses the engineering evaluation of control strategies and technologies used for asbestos removal and management in-place. This program emphasizes (1) improvement of Operation and Maintenance procedures and (2) evaluation of the long-term effectiveness of removal on the decontamination of surfaces, equipment, HVAC systems and building air.

SUPERCRITICAL WATER OXIDATION  
DEEP-WELL REACTOR MODEL DEVELOPMENT

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ABSTRACT

Supercritical water oxidation (SCWO) has the capability of destroying toxic organic compounds. However, to critically evaluate the performance of the SCWO process, extensive information is required on a wide variety of compounds. In addition, engineering problems involving corrosion, heavy metal speciation, ash leachability, charring and encrustation need to be understood.

The main objective of this project is to expand the existing knowledge for the development of the SCWO process. More specifically, the objectives are to: (1) obtain destruction information on five organic compounds, including acetic acid, pentachlorophenol, acenaphthene, 2,4-dinitrophenol (2,4-D) and kepone (chlordecone); (2) conduct detailed kinetic studies for the two most refractory compounds; (3) investigate the corrosion of various metal alloys, and (4) establish the leachability of chromium from effluent ash.

A batch reactor and a continuous-flow reactor system, respectively, are being used to conduct the destruction tests and the detailed kinetic studies. Both of these systems are being used to investigate corrosion and ash leachability. The effects of reaction temperature, waste concentration, oxygen requirements, water density, and retention time are being evaluated. Reaction temperatures range from 400 °C to 500 °C. Oxygen content and water density, respectively, range from 150% to 300% (stoichiometric demand) and from 0.3 g/cm<sup>3</sup> to 0.4 g/cm<sup>3</sup>. The waste and oxidant concentrations and these relationships with retention time are being determined for each compound.

Typical batch test results for the destruction of the selected organic compounds will be presented.

## EXPANSION OF RREL DATA BASE TO INCLUDE SOIL, DEBRIS AND SEDIMENT

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### ABSTRACT

The U.S. Environmental Protection Agency Risk Reduction Engineering Laboratory has developed a computerized database. The database contains information on the treatability of priority pollutants and other hazardous compounds regulated under the Clean Water Act, Safe Drinking Water Act, Resource Conservation and Recovery Act, Toxic Substances Control Act, Superfund Amendments and Reauthorization Act, etc.

The database was initially developed for aqueous wastes but is currently being expanded to include treatability data on soils, sludge, sediment and debris. Distribution of Version 3.0 was initiated in October 1990. This Version contains over 1000 compounds with about 5800 sets of treatability data. Very limited data on soil are contained in this Version. Several sorting capabilities have been programmed into the database which markedly increase its utility.

During the next six to nine months emphasis will be placed upon expanding the data on soil, etc. The database can be obtained free of charge with a written request to:

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Risk Reduction Engineering Laboratory  
26 W. Martin Luther King Drive  
Cincinnati, OH 45268

## **ABSTRACT**

### **ORISMOLOGY: THE NEXT STEP IN QUALITY CONTROL**

by

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Webster defines orismology as "the science of defining technical terms". The area of quality control (QC) has become inundated with scores of new technical terms, and the inconsistent use of these terms has become common. Given the potential for confusion in the application and interpretation of environmental data, orismology has become especially important.

Most QC terms associated with environmental measurements can be grouped into five categories: (1) calibration/standardization, (2) quantitation limits, (3) quality control samples and activities, (4) samples for monitoring measurement performance, and (5) data assessment and reporting. In reviewing over 700 Quality Assurance (QA) Project Plans, as well as experimental designs, sampling/analysis plans, and other technical documents, the Risk Reduction Engineering Laboratory (RREL) has compiled a list of QC-related terms and has attempted to define a uniform system of terminology. Recommended usages of terms and their relationships to QA and QC activities are presented. Also, a discussion of QC procedures and their uses and limitations, is included.

As the next step in quality control, orismology has become important in assuring the correct and comparable use of terminology among the many diverse groups involved in the generation and use of environmental analytical data. Through compilation, definition, and discussion of many of the important technical terms associated with QA/QC of environmental measurements, RREL has attempted to promote the idea of orismology in this area and to encourage the proper and standard use of QC nomenclature.

## RESEARCH OPPORTUNITIES AT EPA'S E-TEC FACILITY

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### ABSTRACT

The EPA Risk Reduction Engineering Laboratory (RREL) has proposed construction of a research facility at Edison, New Jersey for developing, evaluating, and improving technologies for cleaning up Superfund sites. The Environmental Technology and Engineering (E-TEC) facility will be an environmentally safe place for controlled, reproducible tests (up to full scale) on hazardous and toxic materials. It will feature fully permitted, state-of-the-art pollution control equipment to back up the control technology of the hardware being evaluated. This backup capability is such that even if the test equipment fails totally, then E-TEC will still meet all permit conditions and fully protect all employees and citizens.

The facility will be operated by EPA in partnership with the Hazardous Substance Management Research Center of the New Jersey Institute of Technology. This consortium consists of the five major New Jersey universities and over thirty industries involved in the cleanup of hazardous waste sites.

Construction of E-TEC involves renovation of existing warehouse buildings in Edison, New Jersey and the installation of state-of-the-art pollution control equipment. Five separate wastewater treatment systems and two air pollution control systems are proposed. All required federal, state and county permits/approvals will be sought.

A full range of technologies will be able to be tested at E-TEC. They include physical, chemical, thermal and biological testing. No radiological or genetic biological work will be done. The E-TEC testing/evaluation areas are very large, and can accommodate pilot-scale and full scale demonstration projects.

Routine operations at E-TEC are expected to begin in 1994.

ACCESSING LEAKING UNDERGROUND STORAGE TANK CASE STUDIES AND PUBLICATIONS  
THROUGH THE EPA'S COMPUTERIZED ON-LINE INFORMATION SYSTEM (COLIS)

by: R. Hillger  
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ABSTRACT

The U.S. EPA's regulations for underground storage tanks (USTs) require corrective action to be taken in response to leaking USTs. Recent developments of UST programs nationwide as well as the introduction of new technologies to clean up UST sites have increased the diversity of experience levels among personnel involved with this type of work. The EPA's Computerized On-Line Information System (COLIS) has been developed to facilitate technology transfer among the personnel involved in UST cleanup. The system allows for the quick and simple retrieval of data relating to UST incidents, as well as other hazardous waste-related information. The system has been used by response personnel at all levels of government, academia, and private industry. Although it has been in existence for many years, users are just now realizing the potential wealth of information stored in this system. COLIS access can be accomplished via telephone lines utilizing a personal computer and a modem.

## **METAL VALUE RECOVERY FROM ELECTROMACHINING SLUDGE WASTES**

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### **ABSTRACT**

Electrochemical machining sludge wastes are high value materials containing appreciable concentrations of chromium, nickel, cobalt and other elements. Hydrometallurgical processing of these waste materials has been demonstrated to be both technically feasible and economically favorable. Flowsheets, experimental data, and economic evaluations will be presented. The process is presently being refined to improve the selective separability of nickel and cobalt by cyanide complexation followed by selective precipitation. Demonstration of this selective precipitation technique will enhance the economic viability of the treatment process. The results of preliminary experimental test work investigating nickel/cobalt separability by cyanide complexation will be presented and discussed.

BENCH-SCALE WET AIR OXIDATION OF DILUTE ORGANIC  
WASTES AT THE ENVIRONMENTAL PROTECTION AGENCY'S  
TEST AND EVALUATION FACILITY

by

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Wet air oxidation, in conjunction with activated carbon adsorption or biological treatment, has been designated as the best demonstrated available technology (BDAT) for many listed wastes banned from land disposal under the Resource Conservation and Recovery Act (RCRA). A project has been initiated at the U.S. Environmental Protection Agency's Test and Evaluation (T&E) Facility to develop information on the applicability, effectiveness, and costs of wet air oxidation for treating RCRA category P and U wastes.

Wet air oxidation is the oxidative destruction of organics in wastewaters. This technology operates on the principle that oxygen solubility in an aqueous waste is greatly increased at higher pressures, and the oxidation rate of the waste is increased at elevated temperatures. Wastewaters that have been shown to be amenable to such treatment include pesticide production wastes, petrochemical wastes, spent caustic wastewaters containing phenolic compounds, and wastewaters resulting from organic chemical production. Wet air oxidation has typically been applied to the treatment of waste streams containing dissolved or suspended organics with concentrations ranging from 500 to 15,000 mg/L.

The purpose of this research project was to determine the ability to destroy listed organic compounds in wastewaters using wet air oxidation. Bench-scale tests are being conducted at the T&E Facility using a 1-liter autoclave to determine optimum conditions (e.g., pressure, temperature) and obtain kinetic data for destruction of organic wastes by wet air oxidation. The compounds that are being studied (toluene, cyclohexane, and n-dipropylamine) are constituents of listed wastes for which wet air oxidation has been proposed as BDAT by the U.S. Environmental Protection Agency. Cyclohexane and n-dipropylamine have no published kinetic data for wet air oxidation. Studies on toluene only report total batch time, reaction conditions and total destruction. The study will provide the kinetic data required to model and design a wet air oxidation reactor. Preliminary results from the bench-scale wet air oxidation tests are presented for toluene and cyclohexane.

## CHARACTERISTICS OF BEVILL SMELTING WASTES

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### ABSTRACT

In the Hazardous and Solid Waste Amendment of 1984, the Environmental Protection Agency (EPA) was directed to develop regulations to restrict the land disposal of untreated hazardous wastes. Under these requirements, EPA is directed to establish treatment levels or methods based on the standards achieved by treatment technologies for every hazardous waste listing.

In September 1988, the EPA amended its regulations under the Resource Conservation and Recovery Act by reinstating the hazardous waste listings of wastes generated from metal smelting and refining industries. Although these wastes had been listed, the listings were suspended under Section 3001 (b)(3)(A)(ii) (the "Bevill Amendment"). Upon reinterpretation of the statute, the suspensions were removed through court action. The reinterpretation of the Bevill Amendment enacted the original listings and, thus, required the development of treatment standards for the previously exempted listings. Those reinstated wastes were the following:

- K064: Acid plant sludges and slurries produced from the thickening of acid plant blowdown in the manufacture of copper
- K065: Surface impoundment solids contained in and dredged from surface impoundments at primary lead production facilities.
- K066: Sludge from treatment of process wastewater and/or acid plant blowdown from primary zinc production
- K088: Spent potliner from the primary reduction of aluminum.
- K090: Emission control dust/sludge from ferrochromium-silicon production in electric furnaces
- K091: Emission control dust/sludge from ferrochromium production in electric furnaces

The process of developing treatment standards for a hazardous waste listing consists of characterization of the regulated industry and waste, identification of candidate treatment technologies, performance analysis and evaluation of plausible technologies, development of standards, and promulgation of the rule. This poster presents the results (including data) of the engineering site visits, sampling, and analytical information that will be used to support the development of treatment standards for each waste code.

TEST PROGRAM FOR EVALUATION OF FOAM SCRUBBING  
FOR CONTROL OF SUPERFUND TOXIC GAS RELEASES

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ABSTRACT

This poster describes a laboratory-scale test program to evaluate "foam scrubbing" as a technique to mitigate emergency releases of airborne toxics.

In the "foam scrubbing" approach, foam is generated with conventional equipment, actually using the contaminated air to form the foam. The foaming solution contains neutralizing agents and may require a special surfactant system for compatibility. With the airborne gases, vapors, and particulate materials encapsulated in the foam, a large interior liquid surface area is available for their sorption. Neutralization agents present in the bubble walls then react with the entrapped toxic gas or vapor to render it innocuous. The self-collapsing foam yields a processable liquid that may be reusable.

Laboratory-scale tests were carried out using a 2-inch MSA hand-held generator, and a 6-cubic-foot test box. To date, ammonia concentrations ranging from 1 to 20 volume percent have been treated with acid-modified foam, and chlorine concentrations ranging from 1 to 10 volume percent have been treated with base-modified foam.

Ammonia removals of 90 - 100 % were obtained for all starting concentrations, when using stoichiometric amounts of acid. Substantial chlorine removals were obtained for the 1 % and 5 % concentrations, when using stoichiometric amounts of base. Future plans include the addition of thiosulfate to further improve removal of chlorine.

VAPOR-LIQUID EQUILIBRIUM STUDIES  
AT THE U.S. ENVIRONMENTAL PROTECTION AGENCY'S  
TEST AND EVALUATION (T&E) FACILITY

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The Resource Conservation and Recovery Act (RCRA), as amended by the Hazardous and Solid Waste Amendments of 1984, prohibits the placement of RCRA-regulated hazardous wastes in or on the land. Steam stripping has been designated as the best demonstrated available technology (BDAT) for treatment and removal of many of the RCRA-listed wastes that may have been land disposed in the past. The purpose of this research is to provide data that can be used in the design and operation of steam strippers for the treatment of specific RCRA wastes. The research is being conducted at the U.S. Environmental Protection Agency's Test and Evaluation (T&E) Facility in Cincinnati, Ohio.

The design of steam stripping columns requires a characterization of the vapor-liquid equilibrium over the full range of liquid and vapor compositions for the constituents of interest. Stripping columns can be designed by using Henry's Law constants if the solution is sufficiently dilute. Henry's Law data are available for many compounds at low temperatures (20 to 30°C) used in air stripping; however, vapor-liquid equilibrium data are lacking for the high temperature range (90 to 100°C) associated with steam stripping of aqueous wastes at atmospheric pressure. Several chlorinated aromatic compounds and nitroparaffins are of special interest because they are difficult to model accurately due to their limited miscibility with water.

A laboratory-scale Modified Othmer Still apparatus is being used in this research to characterize equilibrium liquid and vapor compositions for organic compounds in aqueous systems. The compounds being tested in the vapor-liquid equilibrium studies are 2-nitropropane, 1,1-dichloroethane, and 2,4-dichlorophenol. Experimental vapor-liquid equilibrium data are unavailable for these industrially significant compounds. The compounds 1,1-dichloroethane and 2,4-dichlorophenol are constituents of EPA Hazardous Waste Codes U076 and U081, respectively. The selected compounds can be analyzed by gas chromatography. Each compound is being tested at atmospheric pressure at several concentrations below the compound's solubility limit. Preliminary results from the vapor-liquid equilibrium studies are presented.

SORPTION ISOTHERMS FOR AZO DYES ONTO ACTIVATED SLUDGE BIOMASS

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ABSTRACT

The Congress of the United States of America enacted the Toxic Substances Control Act (TSCA) in response to the growing numbers of chemicals in contact with humans and the environment, including some substances suspected of presenting an unreasonable risk of injury to human and/or environmental health. According to TSCA, adequate data should be developed with respect to the effect of chemical substances and mixtures on health and the environment. In addition, technological innovation is not to be unduly hindered while ensuring that chemical substances and mixtures do not present an unreasonable risk of injury to health or the environment.

The United States Environmental Protection Agency's Office of Toxic Substances (OTS) is charged with the responsibility to carry out the terms of the Toxic Substances Control Act. This research was conducted to provide OTS with information about an important group of chemical substances known as azo dyes. Sorption is generally considered as the most important process in the removal of azo dyes from wastewater across an activated sludge treatment system. Therefore, sorption isotherms were developed to be used as indicators of the fate of azo dyes treated via the activated sludge process. This poster presents the application of sorption isotherm methodology as a potential tool for the evaluation of azo dyes under the requirements of TSCA.

EPA'S SYNTHETIC SOIL MATRIX (SSM) BLENDING FACILITY

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ABSTRACT

In 1987, a temporary blending facility was constructed at EPA's Center Hill Research Facility in Cincinnati, Ohio for producing a synthetic soil for use as a surrogate test material in waste treatability studies. Since then, work has progressed with the establishment of a permanent blending facility at the EPA's Edison, New Jersey laboratory for continuing the production of this Synthetic Soil Matrix (SSM) for use as a standard test medium in EPA's Superfund Innovative Technology Evaluation (SITE) Program. The SSM is also available to the private sector for use in their development of innovative treatment technologies. The SSM is formulated to represent typical soil types and contaminants found at Superfund sites. Clean soil matrix is created by blending specified amounts of sand, gravel, silt, top soil (for humic content), and a mixture of clays. Water and chemicals (volatiles, semivolatiles, and metals) are added to the soil matrix to simulate environmental contaminants. When performing treatability studies, the synthetic soil matrix provides an effective means for comparing the efficiencies of individual treatment technologies on a common and defined soil matrix.

This presentation describes the Synthetic Soil Matrix Blending Facility which includes a mixing room, personnel decontamination area, and a support area. Capabilities of the facility to produce four standard blends of soil with high and low concentrations of organics and metals, as well as custom blends of other analytes are discussed. Future research efforts to improve the synthetic soil matrix, and to develop a treatment efficiency database from SSM user surveys are also discussed.

RPM/OSC SUMMARY  
REMEDIAL/REMOVAL INCINERATION PROJECTS

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ABSTRACT

The Superfund On Scene Coordinator (OSC) and/or Remedial Project Manager (RPM) must access a wide variety of information when supervising removal/remedial activity at a Superfund site where incineration is to be used. In order to make that information more readily available to the OSC/RPM, the OSC/RPM Summary for Remedial/Removal Incineration Projects was prepared. The document was not intended to be an all inclusive reference on incineration. The body of hazardous waste incineration knowledge changes too rapidly for such a document to be useful for very long. Rather, it was intended to document the OSC/RPM to experts within and outside of the EPA who have the most current knowledge of incineration. Background information on Incinerator Design and Operation, Incinerator Manufacturers and Operators, Incineration Regulations, and Cost is presented concisely and largely in tabular form. Extensive references are provided for more detailed information on the topics discussed in the Document. Together with the lists of incineration experts, the document should provide the OSC/RPM with enough information to more effectively monitor and direct incineration related activities at Superfund sites. This presentation discusses the contents of the Summary document and some of the issues raised during its review.

TREATABILITY STUDY RESULTS ON SOIL CONTAMINATED  
WITH HEAVY METALS, THIOCYANATES, CARBON DISULFATE  
OTHER VOLATILE AND SEMIVOLATILE ORGANIC COMPOUNDS

by: Sarah Hokanson  
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ABSTRACT

Laboratory screening level treatability studies were performed to support the ongoing RI/FS for the Halby Chemical Company site in Wilmington, Delaware. The project team, in coordination with the START team project leader, decided that several technologies were applicable, including combinations of these technologies into treatment trains.

The results from these studies indicate that: (1) aerobic and anaerobic carbon disulfide and aerobic thiocyanate degrading organisms are present in site soils and biodegradation of carbon disulfide and thiocyanate compounds (as indicated by microbial growth and oxygen consumption) can occur in the laboratory with the indigenous microbial population under aerobic conditions with sufficient amounts of nutrients; (2) while low temperature thermal desorption may not be needed as a pretreatment step to solidification/stabilization, it can successfully remove most volatile and semivolatile organic compounds in the site soils at temperatures between 300°F and 500°F and between 15 and 30 minutes residence time; and (3) the soils, themselves, do not leach appreciable amounts of metals under TCLP test conditions and of the binders studied (asphalt and cement), asphalt appears to be the better binder for reducing leachate concentrations of arsenic and copper. Significant flotation/separation of metals from soils using xanthate was not achieved.

## EVALUATION OF TEMPORAL CHANGES IN SOIL BARRIER WATER CONTENT

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### ABSTRACT

The integrity of soil caps and liners in shallow land burial facilities depends on the longterm stability of the barrier water content. Periodic wetting and drying of soil barriers will lead to crack formation and barrier failure. An evaluation of temporal changes in compacted soil barrier water content in representative landfill operations in humid and dry environments is being conducted by computer simulation modelling and with an evaluation of longterm biological activity documented at abandoned landfill sites.

Six water-dynamics models were evaluated for simulation of temporal changes in barrier water content and three were selected for application. The EPA-recommended barrier designs are being evaluated with data from a humid-region site in Tennessee and an arid site in New Mexico using HELP, UTM, and MIGRAT simulation programs. These codes have differing modelling approaches that will be compared in the study. Some initial simulations showed that the penetration of roots into the compacted soil barrier resulted in significant drying, due to transpiration, below the original water content at which the barrier was compacted. Simulation results illustrate the range of variation in barrier water content associated with contrasting climatic regimes.

Ecological succession of local flora and fauna can be expected to result in establishment of deep rooted vegetation and burrowing animals, eventually leading to barrier failure. Different plant and animal species will be active in different climatic, geologic, and ecologic regions of the United States resulting in differing rates of barrier penetration. Measures that may prevent barrier failure by root penetration and animal burrowing should be incorporated into the design and construction of soil-based barriers in waste management structures.

## Abstract

### Evaluation of Stress Cracking Resistance of Polyethylene Flexible Membrane Liners

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The stress cracking resistance of polyethylene flexible membrane liners (FMLs) was evaluated using the notched constant load test (NCLT). The test materials include both high density polyethylene (HDPE) and linear low density polyethylene (LLDPE). For HDPE flexible membrane liners, the conventional test method ASTM D 1693 "Bent Strip Test" was also performed.

The first part of the paper compares the sensitivity between NCLT and the Bent Strip Test. The bent strip test is a qualitative technique. Also the stress relaxation of the polymeric material can influence the outcome of the results, particularly for long testing times. On the other hand, NCLT is a more quantitative test, from which the ductile-to-brittle transition time is obtained. This test overcomes the stress relaxation problem and subjects the test specimens to constant load during the entire test period. The control of the test is more precise than the Bent Strip Test. Also the NCLT is a quantitative test and Bent Strip Test is a qualitative one.

The second part of the paper describes two extrapolation methods used to predict FMLs' behavior at site specific temperatures which are lower than practical laboratory testing temperatures. The two methods are the Rate Process Method (RPM) and Arrhenius modeling. NCLTs are performed at temperatures of 50°C and 75°C in a solution of 10% Igepal and 90% tap water. In addition, a 25°C test is performed so that the predicted data can be compared with the actual experimental results. The results of the second part of the paper further illustrated the power of the NCLT, in that it can be used as a resin qualifying test for stress crack resistance and as a predictive technique to assess polymer aging.

## CENTER HILL SOLID AND HAZARDOUS WASTE RESEARCH FACILITY

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### ABSTRACT

The Center Hill Research Facility provides technical support services in the geo-technical and geo-scientific fields for the Agency's Superfund and Resource Conservation Recovery Act Program activities in solid and hazardous waste testing and research. As one of several pilot-plants supporting the Risk Reduction Engineering Laboratory in Cincinnati Ohio, the Facility houses specialized laboratories with a high bay for testing services and the conduct of research projects at bench, pilot and field scale.

Technical support services by the on-site University of Cincinnati Contractor staff of engineers and scientists focus on soil/chemical/microbiological interactions for pollution control, containment and remediation of the geo-hydrological environment.

Superfund Program activities conducted at Center Hill include technical assistance to the USEPA Regions for site characterization, assessment of proposed remediation technologies, and remedial action program design and construction. In-house computer-aided-engineering services assist the Regions in site-situation mapping and modeling for assessment and monitoring of remedial actions.

RCRA Program activities conducted at Center Hill include the study and evaluation of pollution control technologies for the processing of municipal and industrial solid wastes to control the release of pollutants to the land.

Current research and development activities at Center Hill address the performance of remediation technologies in the Agency's Best Developed Available Technologies (BDAT), Superfund Innovative Technology Evaluation (SITE) and Superfund Technical Assistance Response Team (START) Program areas. Research and development activities are currently being conducted in the area of delivery and recovery systems for in-situ and on-site remediation. A poster and slide presentation will provide a brief description on current project activities.





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